

NATIONAL SCIENCE CURRICULUM MATERIALS

Acids and Bases

R. T. SLATTERY



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NATIONAL SCIENCE CURRICULUM MATERIALS



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Acids and Bases

R. T. Slattery

former Director of NSCM Project

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1
H
1.008

3 Li 6.94	4 Be 9.01
11 Na 23.0	12 Mg 24.3
19 K 39.1	20 Ca 40.1
37 Rb 85.5	38 Sr 87.6
55 Cs 132.9	56 Ba 137.3
87 Fr (223)	88 Ra (226)

89-103	104	105
AC-LW		

89	Ac	(227)
90	Th	232.0
91	Pa	(231)
92	U	238.0
93	Np	(237)
94	Pu	(242)
95	Am	(243)
96	Cm	(248)
97	Bk	(247)
98	Cf	(249)
99	Es	(254)
100	Fm	(253)
101	Md	(256)
102	No	(254)
103	Lw	(257)

Parenthetical values are mass numbers of the isotopes with longest half-lives

INTERNATIONAL WEIGHTS
(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
1	Hydrogen	H	1.008	31	Gallium	Ga	69.72
2	Helium	He	4.003	32	Germanium	Ge	72.59
3	Lithium	Li	6.939	33	Arsenic	As	74.92
4	Beryllium	Be	9.012	34	Selenium	Se	78.96
5	Boron	B	10.81	35	Bromine	Br	79.91
6	Carbon	C	12.01	36	Krypton	Kr	83.80
7	Nitrogen	N	14.01	37	Rubidium	Rb	85.47
8	Oxygen	O	16.00	38	Strontium	Sr	87.62
9	Fluorine	F	19.00	39	Yttrium	Y	88.91
10	Neon	Ne	20.18	40	Zirconium	Zr	91.22
11	Sodium	Na	22.99	41	Niobium	Nb	92.91
12	Magnesium	Mg	24.31	42	Molybdenum	Mo	95.94
13	Aluminium	Al	26.98	43	Technetium*	Tc	(99)
14	Silicon	Si	28.09	44	Ruthenium	Ru	101.1
15	Phosphorus	P	30.97	45	Rhodium	Rh	102.9
16	Sulphur	S	32.06	46	Palladium	Pd	106.4
17	Chlorine	Cl	35.45	47	Silver	Ag	107.9
18	Argon	Ar	39.95	48	Cadmium	Cd	112.4
19	Potassium	K	39.10	49	Indium	In	114.8
20	Calcium	Ca	40.08	50	Tin	Sn	118.7
21	Scandium	Sc	44.96	51	Antimony	Sb	121.8
22	Titanium	Ti	47.90	52	Tellurium	Te	127.6
23	Vanadium	V	50.94	53	Iodine	I	126.9
24	Chromium	Cr	52.00	54	Xenon	Xe	131.3
25	Manganese	Mn	54.94	55	Caesium	Cs	132.9
26	Iron	Fe	55.85	56	Barium	Ba	137.3
27	Cobalt	Co	58.93	57	Lanthanum	La	138.9
28	Nickel	Ni	58.71	58	Cerium	Ce	140.1
29	Copper	Cu	63.54	59	Praseodymium	Pr	140.9
30	Zinc	Zn	65.37	60	Neodymium	Nd	144.2

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

INTERNATIONAL WEIGHTS
(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
61	Promethium*	Pm	(145)	86	Radon*	Rn	(222)
62	Samarium	Sm	150.4	87	Francium*	Fr	(223)
63	Europium	Eu	152.0	88	Radium*	Ra	(226)
64	Gadolinium	Gd	157.3	89	Actinium*	Ac	(227)
65	Terbium	Tb	158.9	90	Thorium*	Th	232.0
66	Dysprosium	Dy	162.5	91	Protactinium*	Pa	(231)
67	Holmium	Ho	164.9	92	Uranium*	U	238.0
68	Erbium	Er	167.3	93	Neptunium*	Np	(237)
69	Thulium	Tm	168.9	94	Plutonium*	Pu	(242)
70	Ytterbium	Yb	173.0	95	Americium*	Am	(243)
71	Lutetium	Lu	175.0	96	Curium*	Cm	(248)
72	Hafnium	Hf	178.5	97	Berkelium*	Bk	(247)
73	Tantalum	Ta	180.9	98	Californium*	Cf	(249)
74	Tungsten	W	183.9	99	Einsteinium*	Es	(254)
75	Rhenium	Re	186.2	100	Fermium*	Fm	(253)
76	Osmium	Os	190.2	101	Mendelevium*	Md	(256)
77	Iridium	Ir	192.2	102	Nobelium*	No	(254)
78	Platinum	Pt	195.1	103	Lawrencium*	Lw	(257)
79	Gold	Au	197.0	104	(Kurchatovium)		
80	Mercury	Hg	200.6				
81	Thallium	Tl	204.4				
82	Lead	Pb	207.2				
83	Bismuth	Bi	209.0				
84	Polonium*	Po	(210)				
85	Astatine*	At	(210)				

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

When you have studied this book, you should know about:

- the Arrhenius, Brönsted-Lowry, and Lewis theories of acid-base reactions;
- the relative strength of acids in terms of the acid constant, K_a ;
- hydrogen ion concentration and the resulting equilibrium constant using indicators;
- the development of the pH theory;
- acid-base strength and structure.

You should be able to:

- interpret acid-base reactions by the Arrhenius, Brönsted-Lowry, and Lewis theories;
- solve problems involving, concentrations, K_a , K_b , K_w , pH, pOH and titration curves.

Introduction

What is an acid?

The answer to this question has exercised the minds of many outstanding scientists for centuries. Anyone who has tasted a lemon will be only too aware of one of the criteria of acidity:

an acid is a substance with a sharp, sour taste

The word “acid” in English is derived from the Latin word *acidus* meaning “sour,” and the German for “acid,” *sauer*, is derived from the old German word *suur* meaning “sour.”

Nitric acid and sulphuric acid were discovered and made during the 13th century. Hydrochloric acid was not discovered till the early part of the 16th century. In the 17th century chemists Johann Glauber (1604–70) and Otto Tachenius (1620–70) acquired extensive knowledge about the properties of acids. Hydrogen chloride, sulphur dioxide, carbon dioxide, and vinegar were recognized as acids. Certain substances such as soda ash and quicklime caused these acids to lose their distinctive properties, and these substances were called bases. These two chemists were the first to observe that salts are the product of the reaction of an acid with a base.

The chemists of the 16th, 17th, and 18th centuries were experimental geniuses. They made many new substances and accumulated a vast quantity of data, which the 19th century chemists used as a basis for building the theories associated with chemistry.

Robert Boyle (1627–91) summarized the then known properties of acids in a paper published in 1663.

Acids are substances which:

- have a sour taste,
- dissolve many substances,
- change blue plant dye to a red colour,
- lose all these properties on contact with bases.

The plant dyes which change colour are now called indicators and many indicators are known that do not come from plants and show other colour changes.

In Boyle’s description of acids, bases have been implicitly defined. The two properties of bases that are emphasized are those

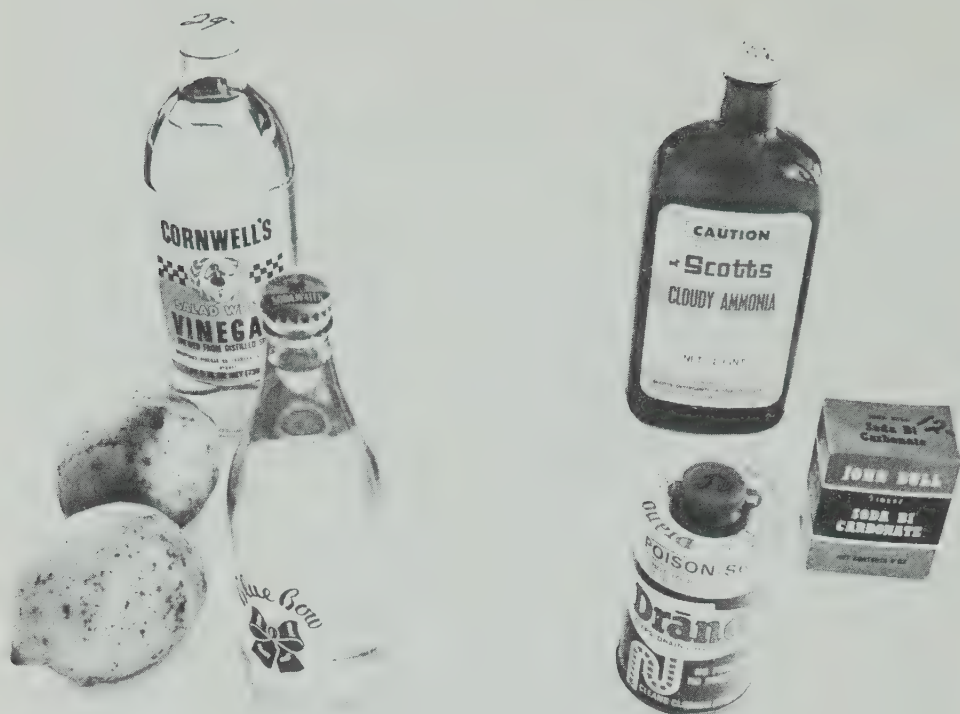


Figure 1. Common acids and bases used in the home

which are opposite to the corresponding properties of acids. Bases in water solution change the red colour of the plant dye, litmus, to a blue colour and bases neutralize the properties of acids. In some way acids and bases may be regarded as opposites and one definition must depend upon the other. This is one aspect of their behaviour that must be explained by any theory of acids and bases.

The Oxygen Theory of Acids

The Frenchman, Antoine Laurent Lavoisier (1743–94), was the first to enquire why acids and bases behave as they do. After the discovery of oxygen by Joseph Priestley in 1774, Lavoisier considered that oxygen was responsible for the acidic properties of acids:

Oxygen is an element common to all acids and the presence of oxygen constitutes or produces their acidity.

Lavoisier said that the oxide of some elements was the true acid. He considered that the hydrogen compounds which are our present-day acids were merely a form of the acid that contained water similar to the water of crystallization observed in many salts.

According to Lavoisier's theory—**The Oxygen Theory of Acids**—carbon dioxide (CO_2) was carbonic acid, sulphur trioxide (SO_3) was sulphuric acid, phosphorus pentoxide (P_2O_5) was phosphoric acid. He regarded organic acids as oxides with the radical, consisting of carbon and hydrogen, being attached to the acidifying principle, oxygen.

Although Lavoisier's Oxygen Theory of Acids was supported by some chemists up to about 1840, it was assailed by contrary evidence almost from its inception. For example, Sir Humphry Davy (1778–1829), the famous English experimentalist, prepared the gas chlorine from hydrochloric acid in 1810 and demonstrated that this acid contained no oxygen. A few years earlier the French chemist, Claude Louis Berthollet (1748–1822), showed that prussic acid (hydrogen cyanide, HCN) and sulphuretted hydrogen (hydrogen sulphide, H_2S) contained no oxygen. The existence of acids without oxygen could no longer be denied. So began a new search for the acidifying principle which oxygen failed to satisfy.

Davy suggested that hydrogen might be the acidifying principle since hydrogen, rather than oxygen, was apparently present in those acids whose composition was known at that time. But even at that time there were many compounds, containing hydrogen, which were not acids and Davy made it quite clear that the acidifying role of hydrogen could not be totally accepted, but that it could be useful. He expressed the opinion that acidity does not depend upon any particular elementary substance but upon peculiar arrangements of various substances.

The Hydrogen Theory of Acids

This theory states that *acids are salts of hydrogen* and was more clearly proposed in 1838 by Justus von Liebig (1803–73), a great German chemist and a pioneer of chemical education. He defined acids as:

compounds containing hydrogen in which hydrogen can be replaced by a metal.

In his search for a comprehensive understanding of acids Liebig recognized the inadequacy of the role supposedly played by water. Acids such as hydrochloric acid, HCl , hydrogen cyanide, HCN , and hydrogen sulphide, H_2S , could not be explained on the basis of water, as no oxygen is present in these compounds. The Liebig definition of an acid in terms of *replaceable hydrogen* gives no clue as to why this kind of combined hydrogen produces the characteristic properties of acids. He was well aware that there were exceptions to his Hydrogen Theory of Acids such as the displacement of hydrogen from substances not then regarded as acids—magnesium with water, and sodium metal with ethanol. Bases were still regarded as substances which neutralized acids to form salts. There was no theory as to the constitution of bases.

About the same time that Liebig's ideas were announced an English scientist, Michael Faraday (1791–1867), one of the experimental geniuses of the 19th century, while working on the passage of electricity through liquids, named acids and bases **electrolytes**—*solutions capable of conducting an electric current*. Faraday's proposal suggested that water solutions of acids and bases became capable of conducting an electric current, by the passage of that current decomposing the substance in solution to electrically charged particles. These charged particles, ions, migrate to the respective electrodes.

Acids and bases now possessed another property—*when in a water solution acids and bases are capable of conducting an electric current*.

The Water Theory of Acids — The Arrhenius Theory

Svante Arrhenius (1859–1927), a Swedish physicist, made investigations on the electrical conductivity of solutions, and in his doctoral thesis of 1884, proposed the partial dissociation of acids, bases, and salts into charged particles when they are dissolved in water.



Figure 2. Svante Arrhenius (1859-1927) was a Swedish physicist and chemist. He studied at the universities of Upsala and Stockholm and at the age of twenty-five he proposed in his doctoral dissertation the partial dissociation of acids, bases, and salts into ions when they are dissolved in water. At first chemists found it difficult to accept his theory; however, it was soon strongly supported by the research of other scientists. In 1903 Arrhenius received the Nobel Prize in chemistry for his dissociation theory and in 1905 became the director of the Nobel Institute for Physical Chemistry, near Stockholm.

This revolutionary idea differed from Faraday's theory in that Arrhenius was saying that the formation of charged particles did not need the passage of an electric current through the solution. The theory of electrolysis is discussed more fully in the NSCM Core Book C11, *Oxidation and Reduction*.

The role of water as an ionizing solvent was emphasized by

Arrhenius and leads to the definition of acids and bases in terms of the ions of water.

An acid is a hydrogen-containing compound that produces hydrogen ions, H^+ , in water.



A base is a hydroxide that dissociates to form hydroxide ions, OH^- , in water.



For example: hydrogen chloride, HCl , sulphuric acid, H_2SO_4 , and acetic acid, CH_3COOH , are acids, while sodium hydroxide, $NaOH$, calcium hydroxide, $Ca(OH)_2$, and nickel hydroxide, $Ni(OH)_2$, are bases.

Arrhenius assumed that the excess hydrogen ions in a water solution of an acid were formed by an equilibrium ionization of the acid as it dissolved in water. For a solution of hydrogen chloride in water, he proposed that the reaction is the dissociation of some of the HCl molecules into positive hydrogen ions, H^+ , and negative chloride ions, Cl^- . These ions are in equilibrium with undissociated hydrogen chloride molecules.



This dissociation theory gives a similar account of the properties of bases in terms of the production of hydroxyl ions, OH^- , in solution, e.g.,



According to the Arrhenius Theory of Acids:

- the strength of an acid is defined in terms of the concentration of hydrogen ions, $H^+_{(aq)}$, present in a water solution of a given concentration of acid.
- the strength of a base is defined in terms of the concentration of hydroxyl ions, $OH^-_{(aq)}$, present in a water solution of a given concentration of base.

Hydrated Hydrogen Ion

Figure 3 illustrates the fact that a hydrogen ion, H^+ , is nothing more than a proton, and consequently it is unique among cations. This cation has no electrons and its effective radius is 10^{-3} pm ($1 \text{ pm} = 10^{-12} \text{ m}$) compared with an effective radius of about 100 pm for other simple cations. Its unit charge and very small

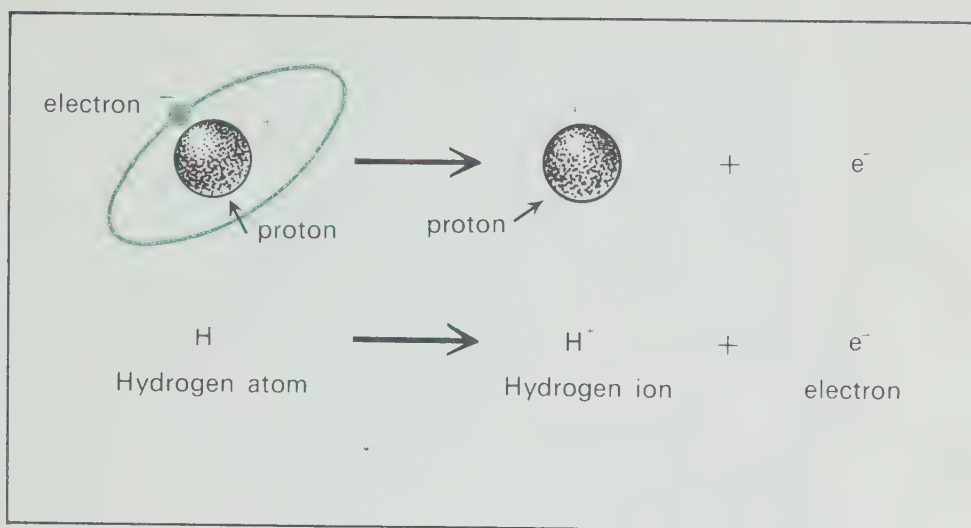


Figure 3. The hydrogen ion is nothing more than a proton

radius give the hydrogen ion a high charge density. The hydrogen ion is quite reactive and will be strongly attracted to molecules which have unshared pairs of electrons.

The proton is surrounded by polar water molecules whose oxygen atoms each bear a partial negative charge as well as two unshared electron pairs (figure 4). This is discussed more fully in the NSCM Core Book C2, *Chemical Bonding*.

It appears certain, therefore, that although the proton can be produced in a discharge tube or in nuclear reactions, and can exist in gases which are under very low pressures, it cannot exist in water. **The proton cannot be responsible for properties of acids in aqueous solution.**

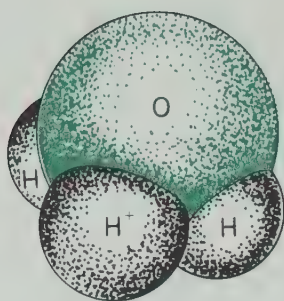
If the hydrogen cation cannot exist unhydrated in water solution we can most logically represent the ionization of hydrogen chloride in water as being an actual reaction with water molecules:



or diagrammatically as in figure 5.

Because of its resemblance to the ammonium cation, NH_4^+ , the hydrated hydrogen cation, $\text{H}_3\text{O}_{(aq)}^+$, is called the hydronium cation, or usually the hydronium ion.

The NSCM Core Books C2, *Chemical Bonding*, and C3, *Chemical Architecture*, have sections on hydrogen bonding, and both discuss the association of water molecules as a result of hydrogen bonding. Each proton is associated with a variable number of molecules of water. The hydrated hydrogen cations in solution are probably



A model of the Hydronium ion, H_3O^+ , is a hydrated proton

H_5O_2^+ , H_7O_3^+ , H_9O_4^+ , etc. The average extent of hydration depends upon the concentration and the temperature.

The formula $\text{H}_3\text{O}_{(aq)}^+$ is customarily used as it is the simplest formula that denotes a hydrated hydrogen cation. In fact the existence of the hydronium ion, H_3O^+ , was proved in 1957 by means of infra-red spectroscopy.

On this basis, the ionization in water of any acid of the form HA can be represented by the general equation:



A classical acid, then, is really a compound which ionizes in water to give hydronium ions.

There are a number of compounds which in water solution exhibit the characteristic properties of bases. In the case of ammonia (NH_3), the other product of the ionization reaction can be shown experimentally to be the ammonium ion, NH_4^+ . The

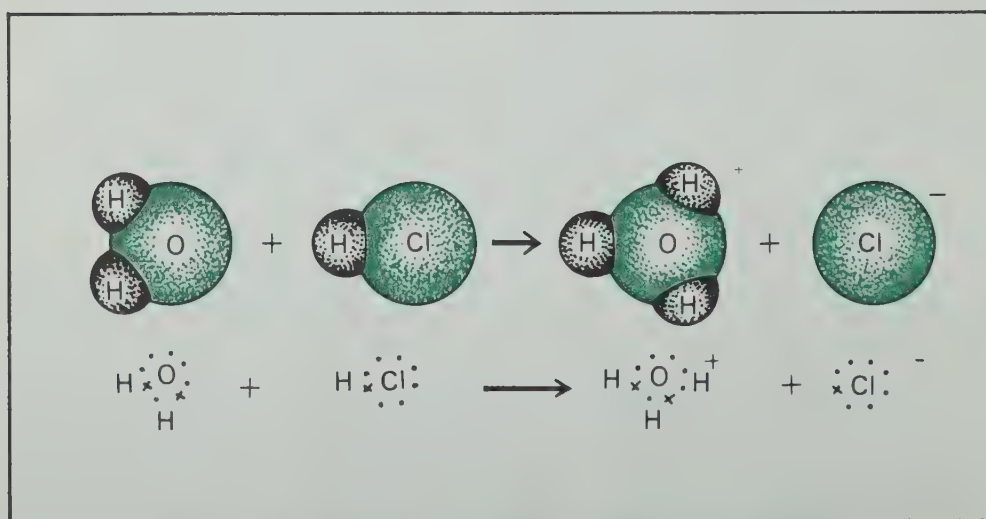


Figure 5. Reaction between water and hydrogen chloride

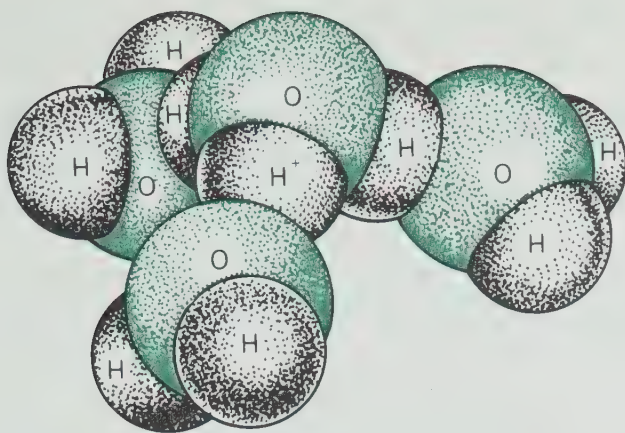


Figure 6. A model of the $H_9O_4^+$ ion, that is, a hydronium ion, H_3O^+ , with three H_2O molecules attached

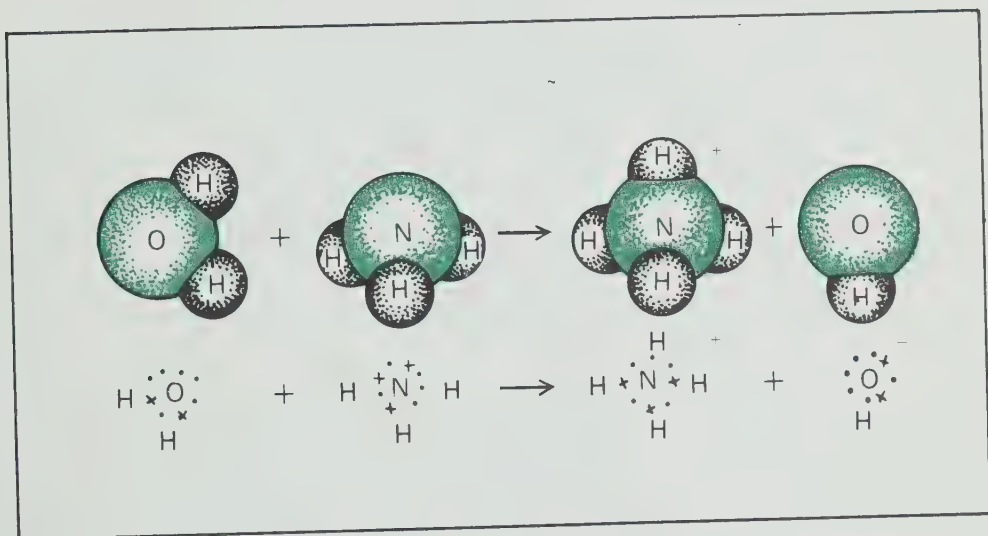
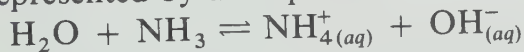


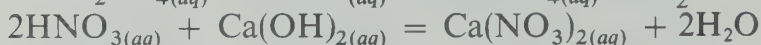
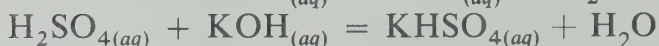
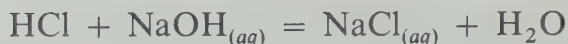
Figure 7. Reaction between water and ammonia

equilibrium reaction involved in the ionization of ammonia in water can be represented by the equation:



Neutralization

An acid-base reaction is the combination of an acid with a base to produce a salt plus water. This reaction is also called a **neutralization** reaction. Typical acid-base reactions are:



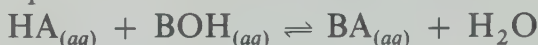
If an acid is expressed by the formula HA, then its dissociation in water is:



If a base is expressed by the formula BOH, then its dissociation in water is:

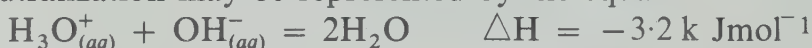


The general equation for an acid-base reaction is:



where BA is the salt formed.

Neutralization may be represented by the equation:



The Arrhenius Theory of Acids was the most important theory of acids and bases for many years, but it is too restrictive. There are many substances which do not contain hydrogen, but which have “acidic” properties, such as: aqueous solutions tasting sour; changing the colours of vegetable dyes; reacting with so-called active metals to produce hydrogen. Aqueous solutions of iron (III) nitrate, $\text{Fe(NO}_3)_3$, aluminium chloride, AlCl_3 , and tin (IV) chloride, SnCl_4 , are acidic. Similarly, there are many substances whose aqueous solutions taste bitter, feel slippery, and neutralize acids—all of which are experimental properties by which bases are identified. Examples are potassium sulphide, K_2S , sodium carbonate, Na_2CO_3 , ammonia, NH_3 , and sodium oxide, Na_2O . Furthermore the Arrhenius definition restricts acids and bases to aqueous solutions, because in this theory the emphasis is on water and reactions in aqueous solution.

The Proton Theory of Acids and Bases — (Brönsted-Lowry Theory)

In 1923, J. N. Brönsted (1879–1947) of Denmark, and T. M. Lowry (1874–1936) of England, independently proposed the theory of acids and bases which now bears both their names. They

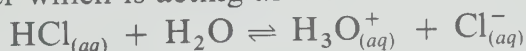
stated that the loss and gain of protons might furnish a basis for classifying substances as acids or bases.

Brönsted and Lowry defined an acid as a proton donor and a base as a proton acceptor.

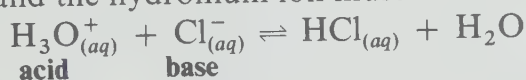
An acid-base reaction can be imagined to be a competition between two chemical species for a hydrogen ion, H^+ . The winner of this competition is called a base and the loser is called an acid.

The base is called a hydrogen ion (proton) acceptor and the acid is called a hydrogen ion (proton) donor.

The reaction of HCl in water is pictured as HCl donating a proton to water which is acting as a base:

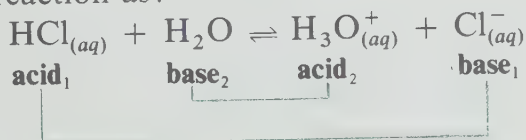


This reaction is reversible as the $Cl^-_{(aq)}$ ion may accept a proton from the $H_3O^+_{(aq)}$ ion and become $HCl_{(aq)}$. The chloride ion must also be a base and the hydronium ion must also be an acid; that is:



Since the $HCl_{(aq)}$ molecule and the $Cl^-_{(aq)}$ ion differ by a proton they are called a **conjugate acid-base pair**. Similarly, the $H_3O^+_{(aq)}$ ion and H_2O molecule are called a conjugate acid-base pair.

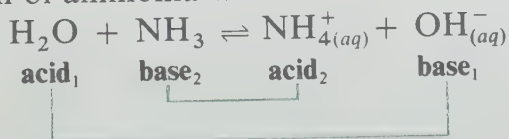
Rewriting the reaction as:



the numbers indicate the conjugate pair. i.e.



For the reaction of ammonia with water:



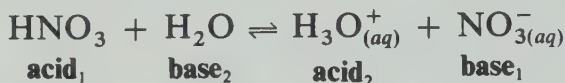
the two conjugate pairs are identified.

According to the Brönsted-Lowry theory water acts as the acid since it transfers a proton to ammonia. That is, water is an acid in this reaction and the negative ion remaining after the proton transfer, the $\text{OH}^-_{(aq)}$ ion, is the conjugate base. Ammonia is the conjugate base of the new acid, $\text{NH}^+_{4(aq)}$. For the reaction of HCl with water, it was shown that water acts as a base since it accepts a proton to form the conjugate acid, $\text{H}_3\text{O}^+_{(aq)}$.

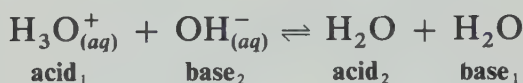
Arrhenius defined an acid as a hydrogen-containing compound that produces hydrogen ions (protons). Since a substance must contain a proton to qualify as a Brönsted-Lowry acid, all Arrhenius acids are also Brönsted-Lowry acids.

Using the Brönsted-Lowry definition, any substance which is capable of donating a proton is an acid. A Brönsted-Lowry acid can be a neutral molecule, a cation, or an anion.

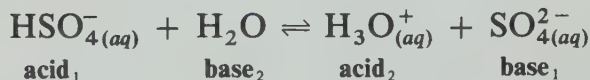
- neutral molecule:



- cation:



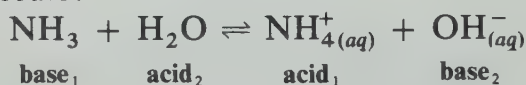
- anion:



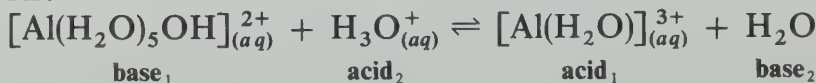
Arrhenius defined a base as a hydroxide that dissociates in water to form hydroxide ions, $\text{OH}^-_{(aq)}$. We have already shown that both NH_3 and $\text{Cl}^-_{(aq)}$ are proton acceptors—Brönsted-Lowry bases.

A Brönsted-Lowry base is a neutral molecule, a cation or an anion which can accept a proton from a Brönsted-Lowry acid.

- neutral molecule:



- cation:



- anion:

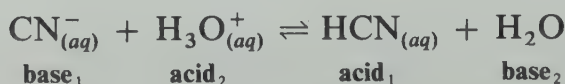


Table 1. Some conjugate acid-base pairs, according to the Brönsted-Lowry theory of acids

Acid	\rightleftharpoons	Proton	+	Base
HNO_3 nitric acid	\rightleftharpoons	H^+	+	NO_3^- nitrate
H_2SO_4 sulphuric acid	\rightleftharpoons	H^+	+	HSO_4^- hydrogen sulphate ion
HSO_4^- hydrogen sulphate ion	\rightleftharpoons	H^+	+	SO_4^{2-} sulphate ion
CH_3COOH acetic acid (ethanoic acid)	\rightleftharpoons	H^+	+	CH_3COO^- acetate ion
$\text{Al}(\text{H}_2\text{O})_6^{3+}$ hexaaquoaluminium ion	\rightleftharpoons	H^+	+	$[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ hydroxopentaaquoaluminium ion
H_2CO_3 carbonic acid	\rightleftharpoons	H^+	+	HCO_3^- hydrogen carbonate ion
H_2S hydrogen sulphide	\rightleftharpoons	H^+	+	HS^- hydrosulphide ion
NH_4^+ ammonium ion	\rightleftharpoons	H^+	+	NH_3 ammonia
HCO_3^- hydrogen carbonate ion	\rightleftharpoons	H^+	+	CO_3^{2-} carbonate ion
H_2O water	\rightleftharpoons	H^+	+	OH^- hydroxide ion
CH_3OH methanol	\rightleftharpoons	H^+	+	CH_3O^- methoxide ion
NH_3 ammonia	\rightleftharpoons	H^+	+	NH_2^- amide ion

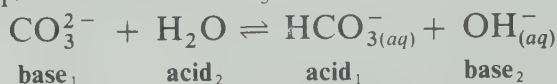
Amphiprotic Substances

Is water an acid or a base?

We have already seen that water acts as a Brönsted-Lowry acid (proton donor) in the NH_3 reaction, and as a Brönsted-Lowry base (proton acceptor) in the HCl reaction. From these two examples it can be seen that the definition of water as an acid or a base depends on the reaction in which it is involved. No attempt should be made to classify water or any substance as a Brönsted-Lowry acid or base, unless the reaction in which it occurs is specified. Substances which are capable of acting as an acid in one reaction and a base in another reaction are called **amphiprotic substances**. Examples of amphiprotic substances are the hydrogen carbonate ion, HCO_3^- , and water.

Hydrogen Carbonate Ion, HCO_3^-

In water the carbonate ion, CO_3^{2-} , accepts a proton according to the given equation and HCO_3^- is a Brönsted-Lowry acid:

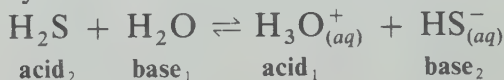


Carbonic acid dissociates into HCO_3^- by loss of a proton and HCO_3^- is a Brönsted-Lowry base:

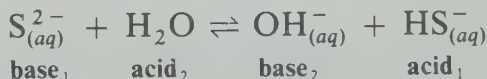


Hydrosulphide Ion, HS^-

In water, hydrogen sulphide, H_2S , donates a proton according to the following equation, and the hydrosulphide ion, HS^- , formed is a Brönsted-Lowry base:



In water the sulphide ion, S^{2-} , accepts a proton according to the following equation, and the hydrosulphide ion, HS^- , formed is a Brönsted-Lowry acid:



Water

The amphiprotic behaviour of water is reflected in the self-dissociation of pure water:

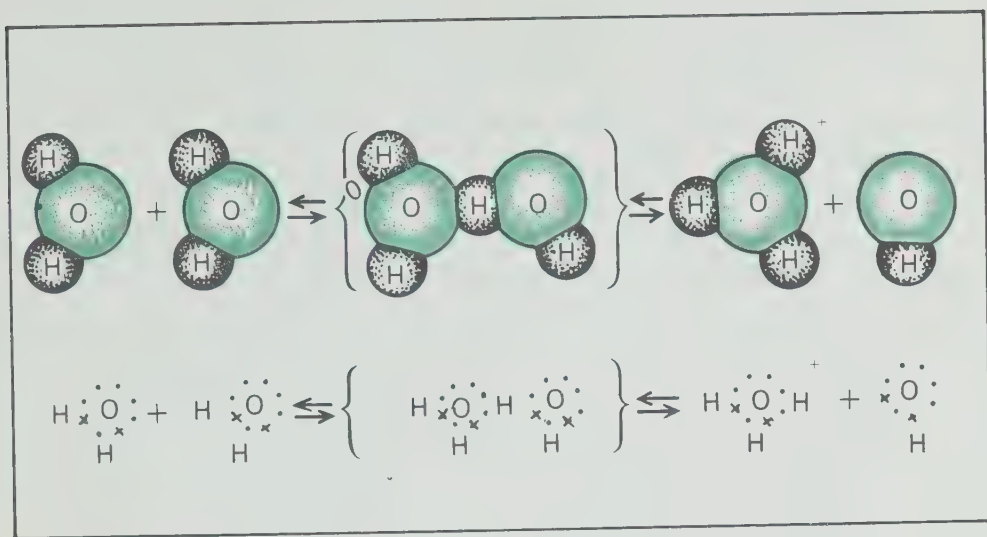
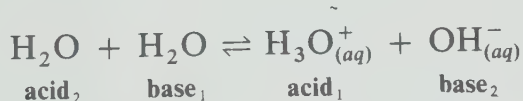


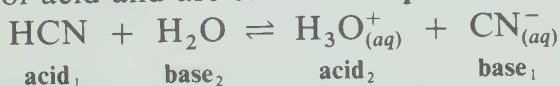
Figure 8. The formation of a hydrogen bond is probably the intermediate step in the self-dissociation of water



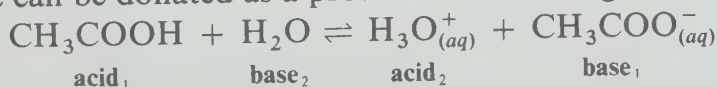
Although the extent of this dissociation is very small, it is a reaction that must always be considered when water is the solvent.

Polyprotic Acids

Acids may be classified in terms of the number of protons per molecule of acid that can be released in a reaction. Acids such as HCl, HNO₃, and HCN contain one ionizable hydrogen atom in one molecule of acid and are called **monoprotic acids**.

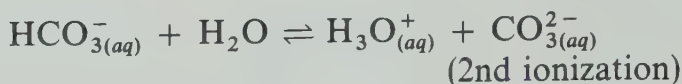
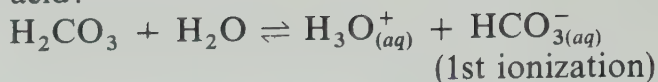


Acetic acid (ethanoic acid) is a monoprotic acid because only one of the four hydrogen atoms which are present in a single molecule can be donated as a proton when reacting with bases.

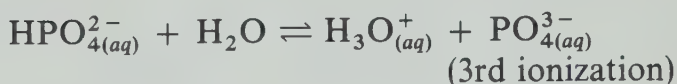
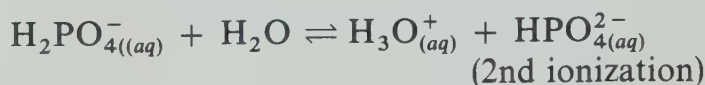
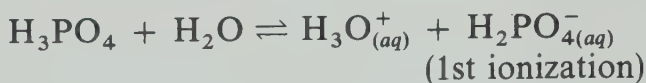


Diprotic acids contain two ionizable hydrogen atoms in one molecule of the acid. Ionization of these acids occurs in two steps. The first ionization, namely loss of one proton, takes place to a greater extent than the second ionization.

For carbonic acid:



Triprotic acids such as phosphoric acid, H_3PO_4 , ionize in three steps:

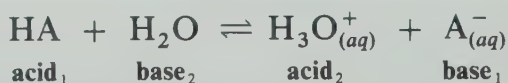


Weak

Strong and Weak Acids

Some acids are described as “**strong**” acids while others are called “**weak**” acids. Since the strength of an acid depends upon the extent to which it reacts with bases the terms “strong” and “weak” are relative. For the Brönsted-Lowry theory it is important that water is used as a reference base in all cases. In other words, *we are comparing all acids by using a standard base.*

The strength of an acid, HA, depends on the concentration of hydronium ions produced in the reaction.



Acid strength can be expressed in terms of the equilibrium constant K_e for the above reaction.

$$K_e = \frac{[\text{H}_3\text{O}_{(aq)}^+] \cdot [\text{A}_{(aq)}^-]}{[\text{HA}] \cdot [\text{H}_2\text{O}]}$$

The concentration of H_2O in a dilute aqueous solution is approximately 55.5 mol l^{-1} , this value being essentially constant for any system in equilibrium. It can therefore be transferred to the

Table 2. Relative strengths of acids in aqueous solution at 298 K

Acid	Strength	Reaction	K_a
HCl	very strong	$\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-_{(aq)}$	very large
HNO_3		$\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^-_{(aq)}$	very large
H_2SO_4		$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-_{(aq)}$	very large
$\text{HSO}_4^-_{(aq)}$	strong	$\text{HSO}_4^-_{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}_{(aq)}$	1.3×10^{-2}
HNO_2		$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-_{(aq)}$	5.0×10^{-4}
HF	weak	$\text{HF}_{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-_{(aq)}$	6.7×10^{-4}
CH_3COOH		$\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-_{(aq)}$	1.8×10^{-5}
H_2CO_3		$\text{H}_2\text{CO}_3_{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-_{(aq)}$	4.4×10^{-7}
$\text{NH}_4^+_{(aq)}$		$\text{NH}_4^+_{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3_{(aq)}$	5.7×10^{-10}
$\text{HCO}_3^-_{(aq)}$		$\text{HCO}_3^-_{(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}_3^{2-}_{(aq)}$	4.7×10^{-11}
H_2O	very weak	$\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-_{(aq)}$	1.8×10^{-16}

left hand side of the equation giving the **acid equilibrium constant**, K_a where:

$$K_a = K_e \cdot [H_2O]$$

$$K_a = \frac{[H_3O^+_{(aq)}] \cdot [A^-_{(aq)}]}{[HA]}$$

An acid which gives a large acid equilibrium constant is called a strong acid. If a high concentration of $H_3O^+_{(aq)}$ is produced in the above reaction, the concentration of unreacted HA is low, and consequently the value of K_a is high—the acid is a strong acid.

If a low concentration of $H_3O^+_{(aq)}$ is produced, the concentration of unreacted HA is high, the value of K_a is low—the acid is a weak acid.

The values of K_a for a number of acids are listed in table 2, and it will be noted that strong acids have large values of K_a . There are no K_a values listed for the strongest acids because these acids dissociate almost 100 per cent in dilute aqueous solutions. The denominator in the above expression would approach zero and result in an infinitely large value of K_a .

Problem

A 0.10 M solution of acetic acid, CH_3COOH , is found to be 1.36 per cent ionized. Calculate the K_a value of the acid.

Solution

The equation for the process is:



$$K_a = \frac{[H_3O^+_{(aq)}] \cdot [CH_3COO^-_{(aq)}]}{[CH_3COOH]}$$

$$[H_3O^+_{(aq)}] = [CH_3COO^-_{(aq)}]$$

$$= 0.10 \times \frac{1.36}{100} \text{ mol l}^{-1}$$

$$= 1.36 \times 10^{-3} \text{ mol l}^{-1}$$

$$[CH_3COOH] = (0.10 - 1.36 \times 10^{-3}) \text{ mol l}^{-1}$$

$$= 9.86 \times 10^{-2} \text{ mol l}^{-1}$$

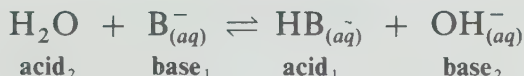
$$K_a = \frac{(1.36 \times 10^{-3})(1.36 \times 10^{-3})}{(9.86 \times 10^{-2})} \text{ mol l}^{-1}$$

$$= 1.85 \times 10^{-5} \text{ mol l}^{-1}$$

Strong and Weak Bases

The strength of a base depends on the extent to which the base reacts with acids. If we use the Brönsted-Lowry definition of a base, we must again select a common acid for comparison of base strengths. The acid commonly used as a reference is, again, water. *Water can either gain or lose a proton so it can be used as a standard acid, much the same as it can be used as a standard base in the previous study of acids.*

The strength of a base, B^- , depends on the concentration of the hydroxyl ions produced in the reaction.



Base strength can be expressed in terms of the equilibrium constant, K_e , for the above reaction:

$$K_e = \frac{[\text{HB}_{(aq)}] \cdot [\text{OH}_{(aq)}^-]}{[\text{B}_{(aq)}^-] \cdot [\text{H}_2\text{O}]}$$

The concentration of water in a dilute solution is essentially constant for any system in equilibrium. It can be absorbed in the equilibrium constant, K_e , giving the base equilibrium constant, K_b .

$$K_b = K_e \cdot [\text{H}_2\text{O}]$$

$$K_b = \frac{[\text{HB}_{(aq)}] \cdot [\text{OH}_{(aq)}^-]}{[\text{B}_{(aq)}^-]}$$

A base which gives a large base equilibrium constant is called a strong base. If a high concentration of $\text{OH}_{(aq)}^-$ is produced in the above reaction, the concentration of unreacted base, $\text{B}_{(aq)}^-$, is low and therefore the value of K_b is high—the base is a strong base.

If a low concentration of $\text{OH}_{(aq)}^-$ is produced, the concentration of unreacted $\text{B}_{(aq)}^-$ is high, the value of K_b is low—the base is a weak base.

The values of K_b for a number of bases are listed in table 3. What do you notice about the K_b values of strong bases? The weak bases have small values of K_b . Notice that there are no K_b values listed for the strongest bases. This is due to the fact that these bases dissociate almost 100 per cent in dilute aqueous solutions.

Table 3. Relative strengths of bases in aqueous solution at 298 K

Base	Strength	Reaction	K_b
$O^{2-}_{(aq)}$	very strong	$O^{2-}_{(aq)} + H_2O \rightleftharpoons OH^{-}_{(aq)} + OH^{-}_{(aq)}$	very large
$NH^{-}_{2(aq)}$		$NH^{-}_{2(aq)} + H_2O \rightleftharpoons NH_{3(aq)} + OH^{-}_{(aq)}$	very large
$OH^{-}_{(aq)}$	strong	$OH^{-}_{(aq)} + H_2O \rightleftharpoons H_2O + OH^{-}_{(aq)}$	9.1
$S^{2-}_{(aq)}$		$S^{2-}_{(aq)} + H_2O \rightleftharpoons HS^{-}_{(aq)} + OH^{-}_{(aq)}$	7.7×10^{-2}
$CO^{2-}_{3(aq)}$		$CO^{2-}_{3(aq)} + H_2O \rightleftharpoons HCO^{-}_{3(aq)} + OH^{-}_{(aq)}$	2.1×10^{-4}
$CN^{-}_{(aq)}$	weak	$CN^{-}_{(aq)} + H_2O \rightleftharpoons HCN_{(aq)} + OH^{-}_{(aq)}$	2.1×10^{-5}
$NH_{3(aq)}$		$NH_{3(aq)} + H_2O \rightleftharpoons NH^{+}_{4(aq)} + OH^{-}_{(aq)}$	1.7×10^{-5}
$HS^{-}_{(aq)}$		$HS^{-}_{(aq)} + H_2O \rightleftharpoons H_2S_{(aq)} + OH^{-}_{(aq)}$	1.1×10^{-7}
$CH_3COO^{-}_{(aq)}$		$CH_3COO^{-}_{(aq)} + H_2O \rightleftharpoons CH_3COOH_{(aq)} + OH^{-}_{(aq)}$	5.9×10^{-10}
$F^{-}_{(aq)}$		$F^{-}_{(aq)} + H_2O \rightleftharpoons HF_{(aq)} + OH^{-}_{(aq)}$	1.5×10^{-11}
$NO^{-}_{2(aq)}$		$NO^{-}_{2(aq)} + H_2O \rightleftharpoons HNO_{2(aq)} + OH^{-}_{(aq)}$	2.0×10^{-11}
$SO^{2-}_{4(aq)}$		$SO^{2-}_{4(aq)} + H_2O \rightleftharpoons HSO^{-}_{4(aq)} + OH^{-}_{(aq)}$	8.3×10^{-13}
H_2O	very weak	$H_2O + H_2O \rightleftharpoons H_3O^{+} + OH^{-}_{(aq)}$	1.1×10^{-15}
$Cl^{-}_{(aq)}$		$Cl^{-}_{(aq)} + H_2O \rightleftharpoons HCl_{(aq)} + OH^{-}_{(aq)}$	very small
$ClO^{-}_{4(aq)}$	extremely weak	$ClO^{-}_{4(aq)} + H_2O \rightleftharpoons HClO_{4(aq)} + OH^{-}_{(aq)}$	very small

Problem

A 0.80 M NH_3 solution is found to be 1.5 per cent ionized. Calculate the K_b value of the base.

Solution

The equation for the process is:



$$K_b = \frac{[\text{NH}_4^+_{(aq)}] \cdot [\text{OH}^-_{(aq)}]}{[\text{NH}_3]}$$

$$[\text{NH}_4^+_{(aq)}] = [\text{OH}^-_{(aq)}]$$

$$= 0.80 \times \frac{1.5}{100}$$

$$= 1.2 \times 10^{-2} \text{ mol l}^{-1}$$

$$[\text{NH}_3] = (0.80 - 1.2 \times 10^{-2}) \text{ mol l}^{-1}$$

$$= 7.88 \times 10^{-1} \text{ mol l}^{-1}$$

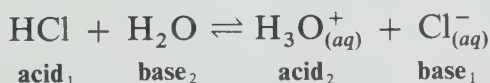
$$K_b = \frac{(1.2 \times 10^{-2}) \cdot (1.2 \times 10^{-2}) \text{ mol l}^{-1}}{(7.88 \times 10^{-1})}$$

$$= 1.83 \times 10^{-5} \text{ mol l}^{-1}$$

Earlier it was stated that a Brönsted-Lowry acid-base reaction may be considered to be a competition between the two bases in the system to accept protons, or between the two acids in the system to donate protons.

The stronger a Brönsted-Lowry acid, the weaker is its conjugate base.

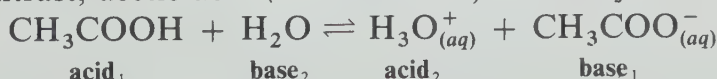
The reaction:



goes nearly to completion, that is, hydrochloric acid is strongly dissociated.

The $\text{Cl}^-_{(aq)}$ ion is the conjugate base of HCl. Since the base, H_2O , won the competition for the proton, it is a stronger base than the $\text{Cl}^-_{(aq)}$ ion. Therefore, $\text{H}_3\text{O}^+_{(aq)}$, the conjugate acid of H_2O , is a weaker acid than HCl, the conjugate acid of the $\text{Cl}^-_{(aq)}$ ion.

In contrast, acetic acid (ethanoic acid) is weakly dissociated:



The $\text{CH}_3\text{COO}^-_{(aq)}$ ion wins the competition for the proton and is, therefore, a stronger base than H_2O . It follows that CH_3COOH ,

the conjugate acid of the $\text{CH}_3\text{COO}^-_{(aq)}$ ion, is a weaker acid than the $\text{H}_3\text{O}^+_{(aq)}$ ion.

On the other hand, *the conjugate base of a weak Brönsted-Lowry acid will always be a strong Brönsted-Lowry base*. Water is a very weak Brönsted-Lowry acid, consequently the $\text{OH}^-_{(aq)}$ ion, the conjugate base of H_2O , is a very strong Brönsted-Lowry base.

Table 2 gives a list of Brönsted-Lowry acids in order of decreasing acid strength and the conjugate base of each acid is also shown. Table 3 gives a similar list of Brönsted-Lowry bases. Notice that in table 2, HCl , a very strong acid, is the conjugate acid of the $\text{Cl}^-_{(aq)}$ ion, which in table 3 is listed as a very weak base. The chloride ion, $\text{Cl}^-_{(aq)}$, is such a weak base that any base below it in the table can take the proton away from the $\text{Cl}^-_{(aq)}$ ion.

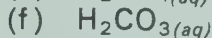
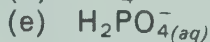
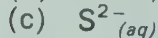
Exercises

- 1 Show by suitable equations that the following chemical species are Brönsted-Lowry bases:
 - (a) $\text{OH}^-_{(aq)}$
 - (b) NH_3
 - (c) $\text{Cl}^-_{(aq)}$
 - (d) $\text{NO}_3^-_{(aq)}$
 - (e) H_2O
- 2 What is the conjugate acid for each of the following Brönsted-Lowry bases?
 - (a) $\text{F}^-_{(aq)}$
 - (b) H_2O
 - (c) $\text{OH}^-_{(aq)}$
 - (d) $\text{HSO}_4^-_{(aq)}$
 - (e) NH_2^-
 - (f) $\text{HCO}_3^-_{(aq)}$
- 3 What is the conjugate base for each of the following Brönsted-Lowry acids?
 - (a) $\text{OH}^-_{(aq)}$
 - (b) $\text{HCO}_3^-_{(aq)}$
 - (c) H_2O
 - (d) $\text{HSO}_4^-_{(aq)}$
 - (e) NH_3
 - (f) $\text{HS}^-_{(aq)}$

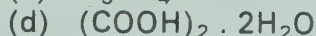
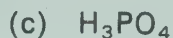
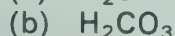
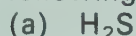
It is implied that each species listed can be considered as a Brönsted-Lowry acid. Is this correct? Explain your answer for each case.
- 4 Write equations for the reaction of the following Brönsted-Lowry acids with water:
 - (a) HNO_3
 - (b) HClO_4
 - (c) $\text{NH}_4^+_{(aq)}$

What is the role played by water in these acid-base reactions?

5 State which of the following species are amphiprotic and write chemical equations showing the amphiprotic character of the chemical species:

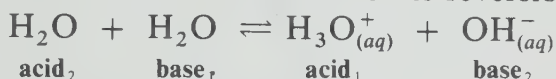


6 Write equations to show the step-wise ionization of the following polyprotic acids:



Water Equilibrium

The hydrated proton $\text{H}_3\text{O}^+_{(aq)}$, present in pure water, comes from the self ionization of water. This reaction is reversible:



The equilibrium constant for this system is:

$$K_c = \frac{[\text{H}_3\text{O}^+_{(aq)}] \cdot [\text{OH}^-_{(aq)}]}{[\text{H}_2\text{O}]^2}$$

The concentration of water remains essentially constant, since water is the solvent that is present in excess. So the equation may be rewritten:

$$K_c \cdot [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+_{(aq)}] \cdot [\text{OH}^-_{(aq)}]$$

where $K_c[\text{H}_2\text{O}]^2$ is a constant and is usually written as K_w , **the water constant**, or **the ion product of water**.

K_w , the water constant, is the product of the equilibrium concentrations of the hydronium ions and the hydroxyl ions. The experimentally determined value for K_w at 298 K is 1.008×10^{-14} . This means that in pure water, or very dilute aqueous solutions, the product of the hydronium ion and hydroxyl ion molarities is $1.008 \times 10^{-14} \text{ mol}^2\text{l}^{-2}$.

The equilibrium concentrations of $\text{H}_3\text{O}^+_{(aq)}$ and $\text{OH}^-_{(aq)}$ must be equal in pure water, i.e.:

$$\begin{aligned}
[\text{H}_3\text{O}_{(aq)}^+] &= [\text{OH}_{(aq)}^-] \\
\text{so that, } [\text{H}_3\text{O}_{(aq)}^+]^2 &= 1.00 \times 10^{-14} \text{ mol}^2 \text{ l}^{-2} \text{ at } 298 \text{ K} \\
\text{that is, } [\text{H}_3\text{O}_{(aq)}^+] &= 1.00 \times 10^{-7} \text{ mol l}^{-1} \text{ at } 298 \text{ K} \\
\text{therefore } [\text{OH}_{(aq)}^-] &= [\text{H}_3\text{O}_{(aq)}^+] \\
&= 1.00 \times 10^{-7} \text{ mol l}^{-1}
\end{aligned}$$

By convention, water is said to be neutral. If $\text{H}_3\text{O}_{(aq)}^+$ is added to water from any source, then the concentration of $\text{H}_3\text{O}_{(aq)}^+$ will be greater than $10^{-7} \text{ mol l}^{-1}$, and, by the above relationship, the concentration of $\text{OH}_{(aq)}^-$ will be less than $10^{-7} \text{ mol l}^{-1}$.

An *acidic solution* is one in which the hydronium ion concentration exceeds $10^{-7} \text{ mol l}^{-1}$ at 298 K.

Acidic solution:

$$[\text{H}_3\text{O}_{(aq)}^+] > 10^{-7} \text{ mol l}^{-1}$$

A *basic solution* is one in which the hydronium ion concentration is less than $10^{-7} \text{ mol l}^{-1}$ at 298 K.

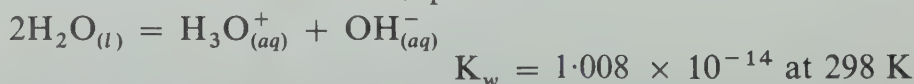
Basic solution:

$$[\text{H}_3\text{O}_{(aq)}^+] < 10^{-7} \text{ mol l}^{-1} \text{ at } 298 \text{ K}$$

Knowing the value of K_w gives us the range over which the concentration of $\text{H}_3\text{O}_{(aq)}^+$ can be measured in water. This range is called acidity of a solution. *Acidity is an important factor which determines the outcome of many chemical reactions.* Chemical reactions in aqueous solutions, including the chemistry of life processes, are very often dependent upon the concentration of hydrogen ions in the solution. The success or failure of many synthetic and analytical processes depends on the hydronium ion concentration. Most chemical industries such as food, petroleum, and drug manufacture continually monitor the acidity of the solutions being used in the preparation of their products. People who own swimming pools carefully control the acidity of the water in the pool in order to destroy harmful bacteria, and to avoid undesirable reactions with the plumbing and plaster.

Variation of K_w with Temperature

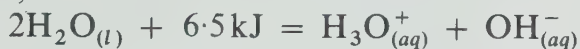
So far we have considered the process:



What happens to the value of K_w if the temperature of the system is

raised above 298 K? What happens if the temperature is lowered below 298 K?

Experiments show that the ionization reaction for water absorbs energy, that is, the reaction is endothermic.



The measured energy term can now be used to predict how K_w changes with temperature. Using the principles developed in the NSCM Core Book C10, *Principles of Chemical Equilibrium*, an increase in temperature of a system shifts the equilibrium in the direction which absorbs the heat energy. In this case an increase in temperature should give a larger concentration of ions, so that K_w should increase as the temperature rises.

Experimental values given in table 4 show that K_w does in fact increase with an increase in temperature. Conversely, decreasing the temperature reduces the concentration of the ions present and so gives a small value of K_w .

Table 4. Values of K_w at various temperatures

Temperature	K_w
273 K	0.114×10^{-14}
283	0.295×10^{-14}
293	0.676×10^{-14}
298	1.008×10^{-14}
303	1.47×10^{-14}
313	2.71×10^{-14}
323	5.30×10^{-14}
333	9.55×10^{-14}
373	100.0×10^{-14}

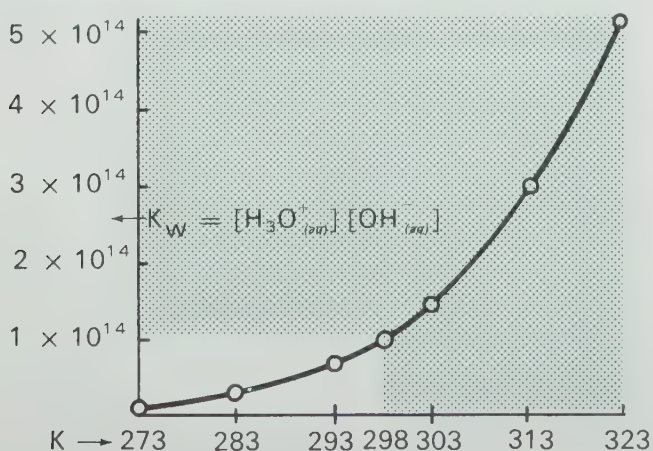


Figure 9. Variation of K_w with temperature

Exercises

- 7 Using the data in table 4, show that the concentration of $\text{H}_3\text{O}^+_{(aq)}$ ions in pure water at 333 K is $3.1 \times 10^{-7} \text{ mol l}^{-1}$. What is the concentration of $\text{OH}^-_{(aq)}$ ions in pure water at 333 K?
- 8 Show that as pure water is warmed from 298 K to 323 K, the concentration of $\text{H}_3\text{O}^+_{(aq)}$ rises from $1.0 \times 10^{-7} \text{ mol l}^{-1}$ to $2.3 \times 10^{-7} \text{ mol l}^{-1}$. Pure water is, by definition, a neutral solution, so this calculation shows that the definition of a neutral solution is not that $[\text{H}_3\text{O}^+_{(aq)}] = 1.0 \times 10^{-7}$ (which applies only at 298 K), but rather that $[\text{H}_3\text{O}^+_{(aq)}] = [\text{OH}^-_{(aq)}]$, which applies at any temperature.

The Meaning of pH

A large number of chemical reactions involve very small concentrations of the hydronium ion. Swimming-pool owners attempt to maintain a hydronium ion concentration of 0.000 000 04 M or $4.0 \times 10^{-8} \text{ M}$. This is an awkward number to use. In 1909, the Danish biochemist, S. P. Sorensen (1868–1939), proposed a more concise method for expressing the acidity of a solution. His proposal was that the acidity of a solution be expressed in terms of a quantity known as pH (**the potency of hydrogen**).

The pH scale is a numerical scale which, for most applications, extends from 0 to 14. The numbers on the scale represent the *relative acidity of solutions* and can be converted to actual hydronium ion concentrations. The midpoint of the scale is taken as 7.0.

- At 298K, a solution with a pH of 7.0 contains equal concentrations of $\text{H}_3\text{O}^+_{(aq)}$ ions and $\text{OH}^-_{(aq)}$ ions and is *neutral*.
- A solution with a pH less than 7.0 has a greater $\text{H}_3\text{O}^+_{(aq)}$ ion concentration than $\text{OH}^-_{(aq)}$ ion concentration and is *acidic*.
- Solutions with pH's above 7.0 have greater $\text{OH}^-_{(aq)}$ ion concentrations than $\text{H}_3\text{O}^+_{(aq)}$ ion concentrations and are *basic*.

The pH scale is represented in figure 10. The pH of a number of common substances is given in table 5.

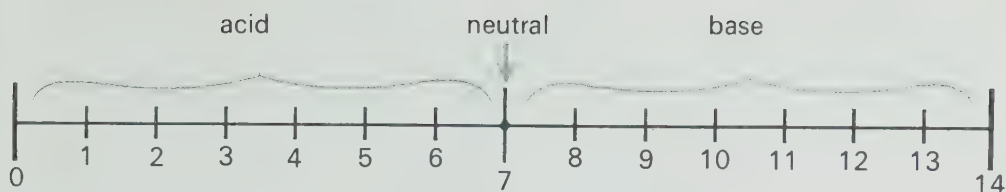


Figure 10. The pH scale at 298K. Most solutions have pH values that range from 0 to 14

Table 5. Approximate pH of some common substances

Substance	pH	Substance	pH
1.0 M HCl	0.0	grapefruit	3.1
0.1 M HCl	1.0	oranges	3.5
gastric juice	2.0	bananas	4.6
lemons	2.3	milk	6.5
vinegar	2.8	pure water	7.0
0.1 M CH_3COOH	2.9	eggs	7.8
soft drinks	3.0	0.1 M NH_3	11.1
apples	3.1	0.1 M NaOH	13.0
		1.0 M NaOH	14.0

The relationship between the pH and the molarity of the $\text{H}_3\text{O}_{(aq)}^+$ ions in a solution is given by:

$$[\text{H}_3\text{O}_{(aq)}^+] = 10^{-\text{pH}}$$

Using logarithmic notation:

$$\text{pH} = -\log [\text{H}_3\text{O}_{(aq)}^+]$$

The relationship between pH and the molar concentration of the $\text{H}_3\text{O}_{(aq)}^+$ ion expressed as a power of ten is shown in table 6.

Careful control of the pH is essential to certain industries and in living organisms. In the brewing industry and in preparation

Table 6. Relationship between $[\text{H}_3\text{O}_{(aq)}^+]$ and pH

Molarity of $\text{H}_3\text{O}_{(aq)}^+$	pH	Condition of Solution
10^0	0	acidic
10^{-1}	1	acidic
$10^{-3.2}$	3.2	acidic
10^{-7}	7	neutral
10^{-9}	9	basic
10^{-14}	14	basic

of penicillin, for example, the pH of the medium is adjusted to encourage growth of the microorganisms (yeasts or moulds). The pH of the blood and other body fluids is normally held closely to values slightly above 7 (the stomach fluids are an exception, having a pH around 2). Sudden changes in the pH, arising either from disease or from ingestion of large quantities of strong acids or strong bases, may cause death.

Problem

Calculate the pH of a solution for which $[\text{H}_3\text{O}_{(aq)}^+] = 4.0 \times 10^{-5} \text{ mol l}^{-1}$.

Solution

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}_{(aq)}^+] \\ &= -\log (4.0 \times 10^{-5}) \\ &= -(0.602 - 5) \\ &= 4.398 \\ &= 4.4 \end{aligned}$$

Problem

Calculate the hydronium ion concentration in a solution which has a pH value of 5.643.

Solution

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}_{(aq)}^+] \\ \text{that is, } \log [\text{H}_3\text{O}_{(aq)}^+] &= -5.643 \\ &= \bar{6}.357 \\ [\text{H}_3\text{O}_{(aq)}^+] &= 2.28 \times 10^{-6} \text{ mol l}^{-1} \end{aligned}$$

Problem

Calculate the pH value of a 0.01 M aqueous solution of CH_3COOH given that the percentage dissociation is 12.5 per cent.

Solution

$$[H_3O^+_{(aq)}] = \frac{12.5}{100} \times 0.01$$
$$= 1.25 \times 10^{-3}$$
$$pH = -\log [H_3O^+_{(aq)}]$$
$$= -\log (1.23 \times 10^{-3})$$
$$= -(0.097 - 3)$$
$$= 2.90$$

The p symbolism is extended to other values. When used in front of symbols or formulas for chemical species, it indicates the negative logarithm of the molar concentration of that species.

pOH

Along with pH it is often convenient to use the symbol pOH. This is defined as the negative logarithm of the hydroxyl ion concentration.

$$pOH = -\log [OH^-_{(aq)}]$$

In water and neutral solutions the pOH is 7. Basic solutions have a pOH less than 7 and acid solutions have a pOH greater than 7. (See figure 11.)

Often this symbolism is used with equilibrium constants to indicate the negative logarithm of the constant as follows:

$$pK_c = -\log K_c$$
$$pK_w = -\log K_w$$

	$[H_3O^+]$ mol / l ⁻¹	pH	$[OH^-]$ mol / l ⁻¹	pOH
Acidic	1	0	10 ⁻¹⁴	14
	10 ⁻¹	1	10 ⁻¹³	13
	10 ⁻²	2	10 ⁻¹²	12
	10 ⁻³	3	10 ⁻¹¹	11
	10 ⁻⁴	4	10 ⁻¹⁰	10
	10 ⁻⁵	5	10 ⁻⁹	9
Neutral	10 ⁻⁶	6	10 ⁻⁸	8
	10 ⁻⁷	7	10 ⁻⁷	7
Basic	10 ⁻⁸	8	10 ⁻⁶	6
	10 ⁻⁹	9	10 ⁻⁵	5
	10 ⁻¹⁰	10	10 ⁻⁴	4
	10 ⁻¹¹	11	10 ⁻³	3
	10 ⁻¹²	12	10 ⁻²	2
	10 ⁻¹³	13	10 ⁻¹	1
	10 ⁻¹⁴	14	1	0

Figure 11. Relationship between [H₃O⁺], [OH⁻], pH and pOH

A useful relationship may be derived from the water constant expression:

$$\begin{aligned}K_w &= [\text{H}_3\text{O}_{(aq)}^+] \cdot [\text{OH}_{(aq)}^-] \\-\log K_w &= -\log ([\text{H}_3\text{O}_{(aq)}^+] \cdot [\text{OH}_{(aq)}^-]) \\&= -\log [\text{H}_3\text{O}_{(aq)}^+] - \log [\text{OH}_{(aq)}^-]\end{aligned}$$

$$\text{that is, } \text{p}K_w = \text{pH} + \text{pOH}$$

since K_w is 1.00×10^{-14} at 298 K, $\text{p}K_w$ is 14 therefore, for aqueous solutions at 298 K:

$$\text{pH} + \text{pOH} = 14$$

This is true in any dilute aqueous solution at 298 K.

A neutral solution is one in which $[\text{H}_3\text{O}_{(aq)}^+] = [\text{OH}_{(aq)}^-]$, or
 $\text{pH} = \text{pOH} = 7.0$ at 298 K

An acid solution is one in which $[\text{H}_3\text{O}_{(aq)}^+] > [\text{OH}_{(aq)}^-]$, or
 $\text{pH} < 7.0$ and $\text{pOH} > 7.0$ at 298 K

A basic solution is one in which $[\text{OH}_{(aq)}^-] > [\text{H}_3\text{O}_{(aq)}^+]$, or
 $\text{pH} > 7.0$ and $\text{pOH} < 7.0$ at 298 K

Problem

What is the pH and pOH for a solution that is 3.6×10^{-8} M in hydroxide ion at 298 K?

Solution

This problem may be solved in two slightly different but related methods.

(i) The pOH may be found directly:

$$\begin{aligned}\text{pOH} &= -\log [\text{OH}_{(aq)}^-] \\&= -\log (3.6 \times 10^{-8}) \\&= -\log (3.6) - \log 10^{-8} \\&= -0.56 + 8 \\&= 7.44\end{aligned}$$

The pH may be found by using the relationship;

$$\begin{aligned}\text{pH} + \text{pOH} &= 14 \\ \text{pH} &= 14 - 7.44 \\ &= 6.56\end{aligned}$$

(ii) The pH may be calculated from the definition, using the equilibrium water constant to find the hydronium ion concentration from the given value for the hydroxide ion concentration:

$$\begin{aligned}
 K_w &= [\text{H}_3\text{O}_{(aq)}^+] \cdot [\text{OH}_{(aq)}^-] \\
 1.0 \times 10^{-14} &= [\text{H}_3\text{O}_{(aq)}^+] \cdot 3.6 \times 10^{-8} \\
 [\text{H}_3\text{O}_{(aq)}^+] &= \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-8}} \\
 &= 2.8 \times 10^{-7} \text{ M} \\
 \text{pH} &= -\log [\text{H}_3\text{O}_{(aq)}^+] \\
 &= -\log (2.8 \times 10^{-7}) \\
 &= -\log 2.8 - \log 10^{-7} \\
 &= -0.44 + 7 \\
 &= 6.56
 \end{aligned}$$

Problem

What is the pH of a 0.05 M NaOH aqueous solution at a temperature of 298 K?

Solution

Since NaOH is completely ionized the concentration of the hydroxide ions is the same as the concentration of NaOH

$$\begin{aligned}
 [\text{OH}_{(aq)}^-] &= 0.05 \\
 &= 5 \times 10^{-2} \text{ M} \\
 \text{pOH} &= -\log [\text{OH}_{(aq)}^-] \\
 &= -\log (5 \times 10^{-2}) \\
 &= -\log 5 + 2 \\
 &= 2 - 0.7 \\
 &= 1.3 \\
 \text{pH} + \text{pOH} &= 14.0 \\
 \therefore \text{pH} &= 12.7
 \end{aligned}$$

Problem

How many grams of NaOH will need to be dissolved in 10 l of water to make a solution whose pH is 9.0?

Solution

$$\begin{aligned}
 \text{pH} &= -\log [\text{H}_3\text{O}_{(aq)}^+] \\
 9 &= -\log [\text{H}_3\text{O}_{(aq)}^+] \\
 \therefore [\text{H}_3\text{O}_{(aq)}^+] &= 10^{-9} \\
 K_w &= [\text{H}_3\text{O}_{(aq)}^+] \cdot [\text{OH}_{(aq)}^-] \\
 1.0 \times 10^{-14} &= 10^{-9} [\text{OH}_{(aq)}^-] \\
 [\text{OH}_{(aq)}^-] &= 1.0 \times 10^{-5} \text{ mol l}^{-1}
 \end{aligned}$$

alternatively:

$$\begin{aligned}\text{pH} &= 9 \\ \text{pOH} &= 14 - 9 \\ &= 5 \\ \text{pOH} &= -\log [\text{OH}^-_{(aq)}] \\ [\text{OH}^-_{(aq)}] &= 1.0 \times 10^{-5} \text{ mol l}^{-1}\end{aligned}$$

Since NaOH is completely dissociated the concentration of NaOH will be $1.0 \times 10^{-5} \text{ mol l}^{-1}$.

In 10 l of solution there will be $1.0 \times 10^{-4} \text{ mol}$ of NaOH.

$$\begin{aligned}\text{amount of NaOH} &= (\text{no. of mole}) \times (\text{mol. wt.}) \\ &= 1.0 \times 10^{-4} \times 40 \\ &= 4.0 \times 10^{-3} \text{ g}\end{aligned}$$

The Range of pH

We are accustomed to seeing pH values ranging between the limits $\text{pH} = 0$ and $\text{pH} = 14$. However these values do not represent the limiting extremes. Two examples will be used to illustrate this argument.

Problem

Calculate the pH of a 2.0 M aqueous solution of HNO_3 .

Solution

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 2.0 \text{ mol l}^{-1} \\ \text{pH} &= -\log [\text{H}_3\text{O}^+_{(aq)}] \\ &= -\log 2 \\ &= -0.3\end{aligned}$$

Problem

Calculate the pH of a 5.0 M aqueous solution of NaOH given that $\text{pK}_w = 14.0$.

Solution

$$\begin{aligned}[\text{OH}^-_{(aq)}] &= 5 \text{ mol l}^{-1} \\ \text{pOH} &= \log [\text{OH}^-_{(aq)}] \\ &= \log 5 \\ &= 0.70 \\ \text{since } \text{pH} + \text{pOH} &= \text{pK}_w \\ \text{that is, } \text{pH} + (0.70) &= 14.0 \\ \text{pH} &= 14.7\end{aligned}$$

The conclusion to be drawn is that in dilute solutions the pH may range between 0 and 14. In concentrated acid solutions the pH is negative (the effective pH of concentrated H_2SO_4 is of the order, $\text{pH} = -10$). In concentrated aqueous solutions of NaOH or KOH, the effective pH has been estimated to have a value of approximately $\text{pH} = 18$.

What is a Neutral Solution?

If a solution has a pH of 7.0 is it a neutral solution? A neutral aqueous solution is defined as one in which the concentration of the hydronium ions equals the concentration of the hydroxyl ions.

$$[\text{H}_3\text{O}_{(\text{aq})}^+] = [\text{OH}_{(\text{aq})}^-]$$

that is $\text{pH} = \text{pOH}$

The value of K_w at 298 K is given in table 4 as 1.00×10^{-14}

$$\text{p}K_w = 14.0$$

For aqueous solutions at 298 K:

$$\text{pH} + \text{pOH} = \text{p}K_w$$

For a neutral aqueous solution:

$$\begin{aligned} 2\text{pH} &= \text{p}K_w \\ \text{pH} &= \frac{1}{2}\text{p}K_w \\ &= 7.0 \end{aligned}$$

As a useful approximation, in aqueous solutions at 298 K, a pH value of 7.0 represents a dividing line with lower pH values indicating acidic and higher pH values, basic solutions.

It must not be inferred from this that a pH of 7.0 defines a neutral solution in all cases. The value of K_w changes with temperature (refer to table 4 on page 25) and other factors not discussed in this book. Therefore the pH of a neutral aqueous solution will change accordingly.

Problem

What is the pH of pure water at 373 K?

Solution

From table 4:

$$\begin{aligned} K_w &= 100 \times 10^{-14} \text{ at } 373 \text{ K.} \\ &= 10^{-12} \\ \text{p}K_w &= 12.0 \end{aligned}$$

The pH of a neutral solution is $\frac{1}{2}pK_w$.

$$\frac{1}{2}pK_w = 6.0$$

that is, $pH = 6.0$

It is of interest to notice that although this water solution is neutral, it has a significantly higher hydronium ion concentration than water at 298 K.

To assist us in visualizing the way in which $[H_3O^+_{(aq)}]$ and $[OH^-_{(aq)}]$ vary in all aqueous solutions study figure 12 in which the logarithms of the concentration of these ions are plotted against pH.

The line representing $\log [H_3O^+_{(aq)}]$ is the graphical form of the equation:

$$\log [H_3O^+_{(aq)}] = -pH$$

The line representing $\log [OH^-_{(aq)}]$ is obtained from the equation:

$$\begin{aligned} \log [OH^-_{(aq)}] &= -pOH \\ &= pH - pK_w \end{aligned}$$

The pH of a neutral solution is the value at which these two lines intersect.

Problem

Calculate the hydronium ion concentration and the pH value of a 1.0×10^{-1} M solution of perchloric acid, $HClO_4$, on progressive dilution with pure water at 298 K.

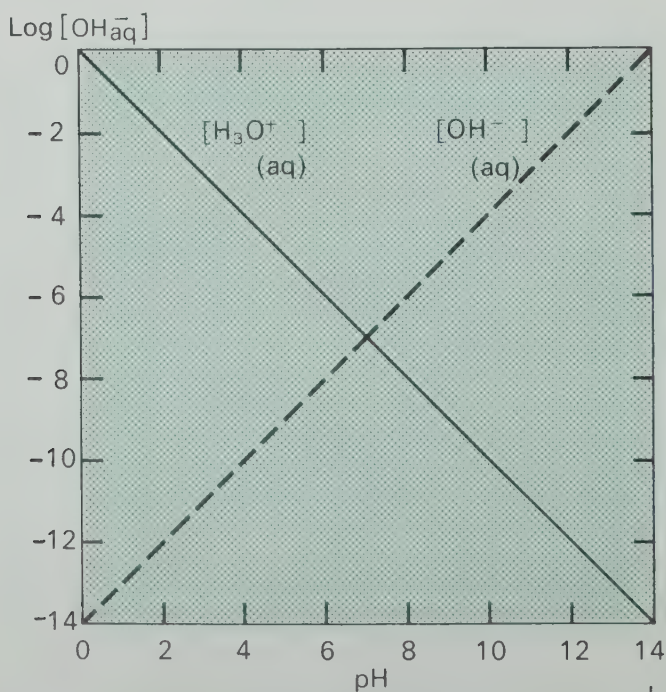


Figure 12. Variation of $\log [H_3O^+_{(aq)}]$ and $\log [OH^-_{(aq)}]$

Solution

Molarity of HClO_4	$[\text{H}_3\text{O}_{(aq)}^+]$	pH
1.0×10^{-1}	1.0×10^{-1}	1.0
1.0×10^{-3}	1.0×10^{-3}	3.0
1.0×10^{-5}	1.0×10^{-5}	5.0
1.0×10^{-8}	?	?

If the perchloric acid solution is diluted until the molarity of the HClO_4 is 1.0×10^{-8} , the pH of the solution is **certainly not** 8.0, as this would mean that a basic solution has been obtained by diluting a solution of a strong acid.

The pH of the solution can never be greater than 7.0 since the $[\text{H}_3\text{O}_{(aq)}^+]$ cannot be less than that present in pure water.

On progressive dilution of the HClO_4 solution its concentration of hydronium ions reaches a limiting value of 1.0×10^{-7} and the pH of the solution levels off at a value of 7.0.

The conclusion to be drawn from the above problem is that in extremely dilute aqueous solutions of strong acids, the hydronium ions contributed by water must be taken into account.

Exercises

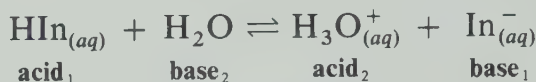
- 9 Calculate the pH of a solution in which the $[\text{H}_3\text{O}_{(aq)}^+]$ equals
 - (a) 1.0 M
 - (b) 0.1 M
 - (c) 0.01 M
 - (d) 1.0×10^{-7} M
 - (e) 3.0×10^{-7} M
 - (f) 4.0×10^{-10} M
- 10 What is the pOH of each of the solutions in exercise No. 9?
- 11 What is the pH of a solution that contains 1×10^{-8} mol of $\text{OH}_{(aq)}^-$ per litre of solution?
- 12 Calculate the pH of 50 ml of 0.25 M HNO_3 aqueous solution. What is the pH of 100 ml of this 0.25 M HNO_3 aqueous solution? Show that the pH of 100 ml of 0.25 M HNO_3 aqueous solution changed by +1 if it is diluted with pure water to a volume of 1000 ml.

Measurement of pH

There are a number of experimental methods for determining the pH of a solution. Some of these are very precise and involve instruments or complex procedures. One of the simplest methods involves the use of indicators.

Acid-Base Indicators

Acid-base indicators are organic compounds with complex structures, having colours that are sensitive to the hydronium ion concentration. Many acid-base indicators are weak acids with an idealized formula, HIn , which ionize according to the following equation:



The un-ionized acid, HIn , has one colour whilst the conjugate base, $\text{In}_{(aq)}^-$, has another colour.

Phenolphthalein

Let us illustrate indicator action with an indicator in common use. One indicator acid is phenolphthalein which we will denote by the formula given above, namely HIn . The un-ionized acid, HIn , is colourless and the conjugate base, $\text{In}_{(aq)}^-$, has a deep red coloration.

The acid equilibrium constant is given by the expression:

$$K_a = \frac{[\text{H}_3\text{O}_{(aq)}^+] \cdot [\text{In}_{(aq)}^-]}{[\text{HIn}_{(aq)}]}$$

$$\text{that is, } \log K_a = \log [\text{H}_3\text{O}_{(aq)}^+] + \log \frac{[\text{In}_{(aq)}^-]}{[\text{HIn}_{(aq)}]}$$

Using the p notation:

$$\text{p}K_a = \text{pH} - \log \left(\frac{[\text{In}_{(aq)}^-]}{[\text{HIn}_{(aq)}]} \right)$$

re-arranging this expression:

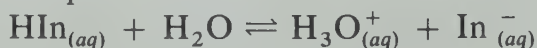
$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{In}_{(aq)}^-]}{[\text{HIn}_{(aq)}]} \right)$$

In extremely dilute solutions the red colour of the conjugate base occurs when $[\text{In}_{(aq)}^-] = [\text{HIn}_{(aq)}]$

then, $\text{pH} = \text{p}K_a$

Since $\text{p}K_a$ indicates the pH it is given the symbol $\text{p}K_{ind}$ and is called the indicator constant.

Phenolphthalein has a $\text{p}K_{ind}$ value of 9.3. If an acid-base indicator is placed in a solution with a certain hydronium ion concentration, the equilibrium of the indicator system may be shifted to the left of the equation:



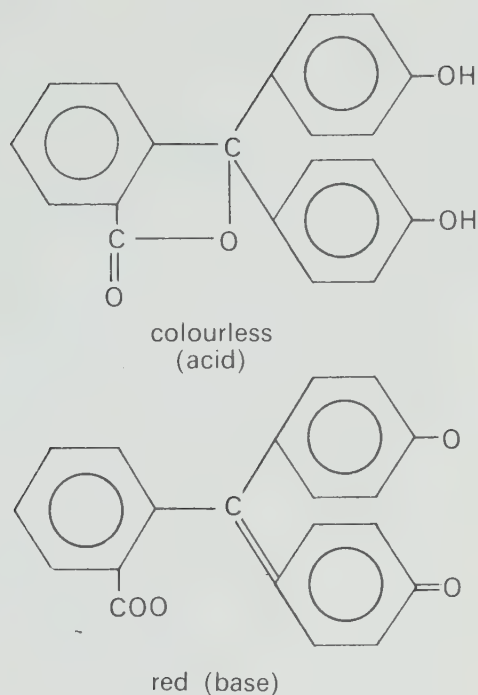


Figure 13. The change in structure of phenolphthalein from an acid solution to a basic solution

so that the colour of the un-ionized acid, HIn , will predominate.

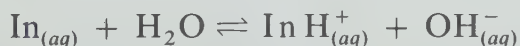
On the other hand, the solution may have sufficiently low hydronium ion concentration, and the conjugate base of the acid indicator predominates with its characteristic colour.

The colour change of an indicator involves more than ionizing a weak acid or hydrolysing the conjugate base of that weak acid. The change in the structure of phenolphthalein is shown in figure 13.

Notice that there is a rearrangement of bonds as well as a loss of hydrogen ions in going from the colourless acid to the red-coloured conjugate base.

Methyl Orange

Methyl orange is a weak organic base which is used as an acid-base indicator. Let us denote the un-ionized base, methyl orange, by the symbol, In . Then ionization may be shown by the following equation:



The un-ionized base, In , has a light yellow colour and the conjugate acid, $\text{InH}_{(aq)}^+$, has a red colour. There are a great many acid-base indicators; some of these are listed in table 7 and illustrated in figure 14.

Table 7. Some acid-base indicators

Common name	Transition	Colour change	
	range, pH	Acid	Base
methyl violet	0.5–1.5	yellow	blue
thymol blue	1.2–2.8	red	yellow
bromophenol blue	2.7–4.6	yellow	blue
methyl orange	3.1–4.4	red	yellow
bromocresol green	3.8–5.4	yellow	blue
methyl red	4.2–6.3	red	yellow
chlorophenol red	4.8–6.4	yellow	red
bromthymol blue	6.0–7.6	yellow	blue
phenol red	6.4–8.0	yellow	red
neutral red	6.8–8.0	red	yellow-orange
phenolphthalein	8.0–9.6	colourless	red
thymolphthalein	9.3–10.5	colourless	blue
alizarin yellow	10.1–12.0	colourless	violet

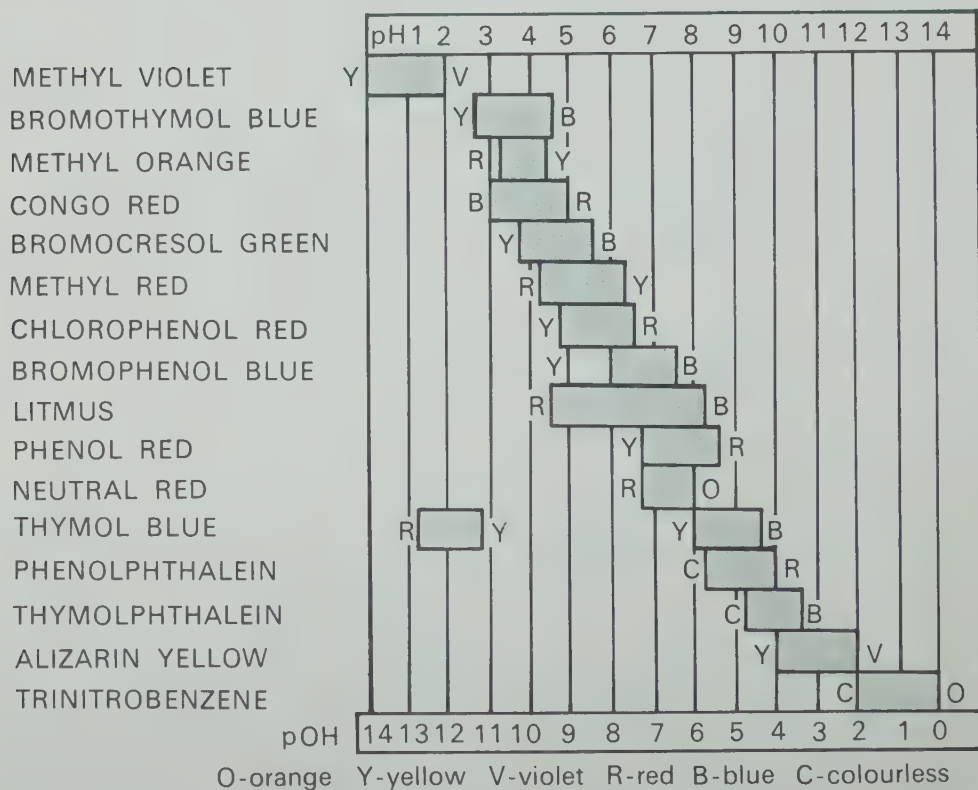


Figure 14. pH range in which some common acid-base indicators change colour

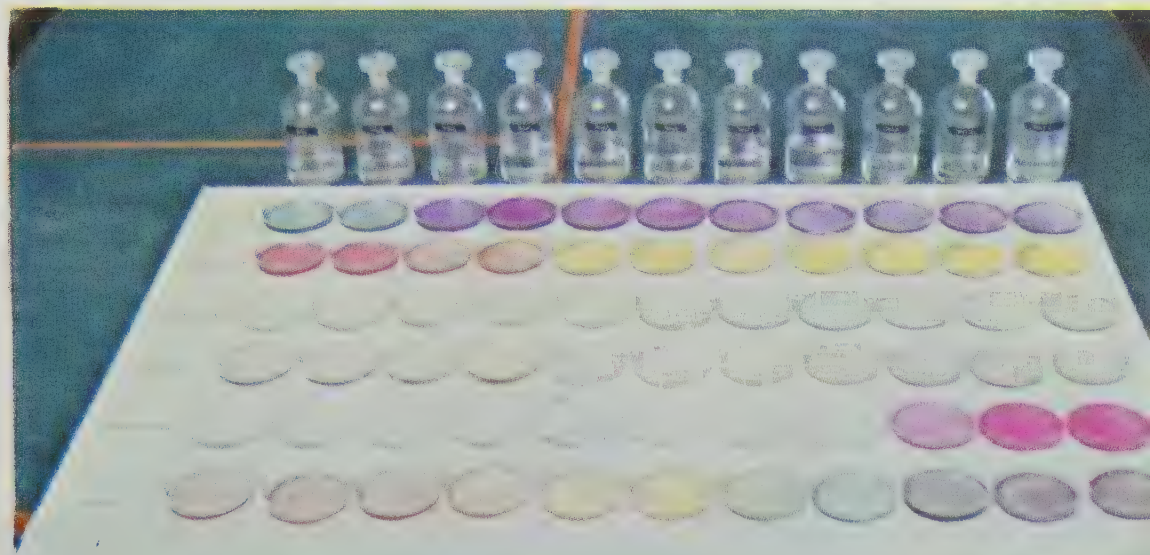
We see from table 7 and figure 14 that the colour change is not a sharp one but takes place over a small range of pH. By using a combination of indicators, the pH of a solution can be located within very narrow limits. For example, if a drop of solution turns violet upon addition of a drop of methyl violet then the pH is greater than 2.0. On the other hand if another drop of the same solution turns red upon the addition of a drop of methyl orange, we know that the pH is less than 3.0. Therefore we know that the pH of the solution is between 2.0 and 3.0. Other indicators might make it possible to find the pH to within even narrower limits.

For a compound to function satisfactorily as an acid-base indicator, the visible change observed should satisfy the following conditions:

- the change should be a distinct one and should occur over the shortest possible pH range;
- the indicator change should be reversible and the reaction involved should be rapid in both directions;
- the indicator should be sensitive; that is, only a small quantity should be required to impart a distinct colour to the solution being tested;
- the presence of the indicator in a solution should not appreciably affect the hydronium ion concentration of the solution.

For approximate determination of pH, universal indicators are useful. These are mixtures of indicators whose combined colour changes occur over a wide pH range. One such universal indicator is made from methyl orange, methyl red, bromothymol blue and phenolphthalein. Figure 15 shows the colours that are obtained with acid-base indicators at different pH values.

Figure 15. Variation of acid-base indicator colours with changing hydronium ion concentration



Exercise

- 13 Using the data given in table 7 determine the pH limits of solutions which exhibit the indicated colours with the following pairs of indicators:
- (a) a solution which turns methyl violet a violet colour and methyl red a red colour.
 - (b) a solution which turns thymol blue a yellow colour and litmus a red colour.
 - (c) a solution which turns phenolphthalein a red colour and trinitrobenzene colourless.
 - (d) a solution which turns methyl violet a violet colour and congo red a blue colour.
 - (e) a solution which turns thymol blue a yellow colour and methyl red a red colour.

The pH Meter

The most precise method of measuring pH is by means of a glass electrode. Glass has the property of being slightly permeable to hydrogen ions. The potential difference between the inner and outer surfaces depends on the relative concentrations of hydronium ions in contact with these surfaces.

The pH meter consists of an electrochemical cell containing two electrodes immersed in a solution and connected to a millivoltmeter calibrated in pH units.

The glass electrode (G_e) half-cell consists of an internal electrode, E_i , permanently immersed in a solution containing a constant and known concentration of $H_3O^+_{(aq)}$ ions, (F). The emf developed between E_i and G_e is constant under all half-cell conditions. The solution (F) is contained in a thin membrane of special glass (L). When the electrode is placed in a solution, an emf is developed across the glass membrane. The value of this emf is a function of the difference in the $[H_3O^+_{(aq)}]$ of the solutions on either side of the glass membrane.

The purpose of the reference electrode (R_e) half-cell is to complete the electrochemical cell containing two half-cells. The reference electrode has an internal electrode, E_{ii} , immersed in a solution of definite composition (H). The emf developed between E_{ii} and H is constant. Contact between the solution H, and the

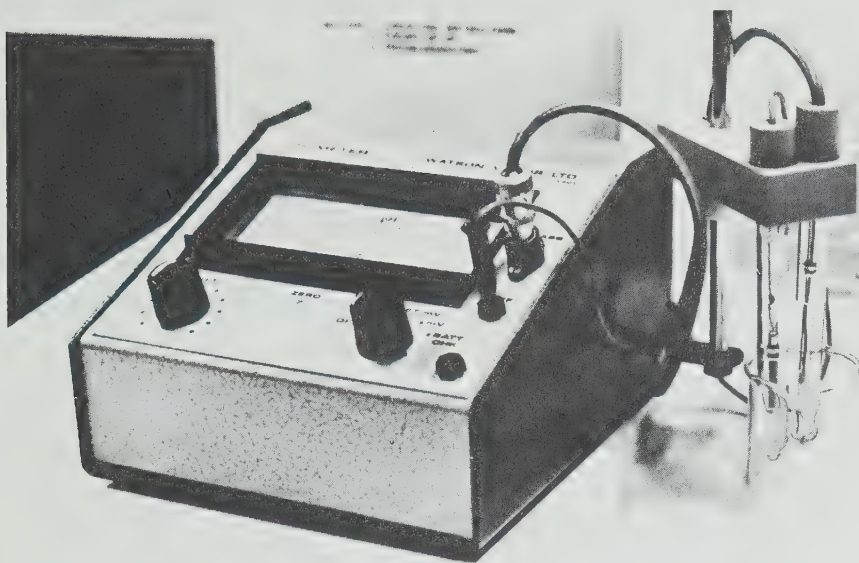
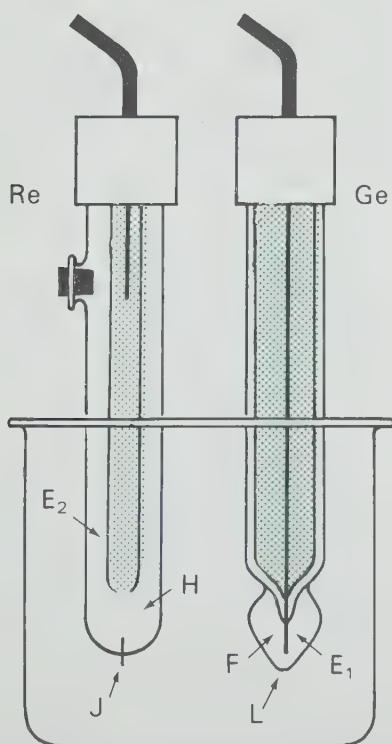


Figure 16. A pH meter. The potential across the glass electrode varies with the $[H_3O_{(aq)}]$ of the solution



TYPICAL ELECTRODE SYSTEM FOR THE POTENTIOMETRIC MEASUREMENT OF pH

Figure 17. Typical electrode system for the potentiometric measurement of pH

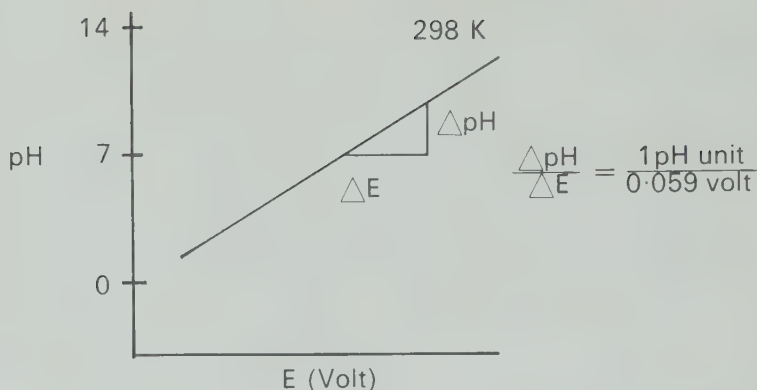


Figure 18. Graphical relationship between cell potential and pH of a solution

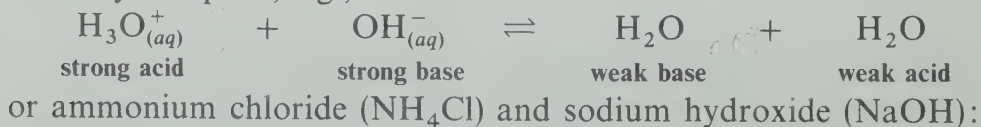
solution whose pH is to be measured, is through a small hole, J, at the bottom of the electrode.

The two electrodes placed in the solution and the electrical meter complete the electrochemical cell called the pH meter. The relationship between the electrochemical cell potential and the pH of the solution is a linear one; the slope of the line is dependent on the temperature. At 298 K the slope of the line in figure 18 is 1 pH unit per 0.059 volt, so that each pH unit on the scale of the meter is equivalent to 0.059 V.

Acid-Base Reactions

Strong Acid—Strong Base Reactions

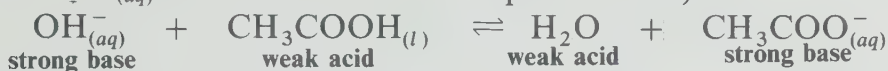
The strength of an acid or base is measured by its tendency to lose or gain protons. A strong acid loses its proton easily; therefore, its conjugate base is weak. A strong base will have a strong attraction for protons and its conjugate acid will, therefore, be weak. When a strong acid and a strong base combine, the reaction is virtually complete, e.g., NaOH and HCl:



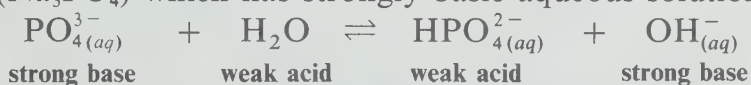
Even if NH_3 were not volatile, this reaction would go far toward completion.

Weak Acid—Strong Base Reactions

Competition for protons may result when a strong base reacts with a weak acid. For example, if NaOH is added to CH_3COOH (where $\text{Na}^+_{(aq)}$ ion is considered as a spectator ion):



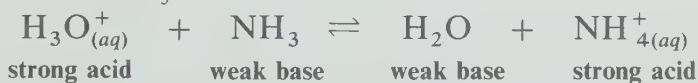
Because the strong base that is produced can pull protons from water, this reaction is somewhat reversible. Therefore, when one mole of CH_3COOH is added to one mole of NaOH , the final solution still contains some $\text{OH}^-_{(aq)}$ ions and is basic. If a mole of sodium acetate is added to water, precisely the opposite reaction occurs with the Na^+ ion as spectator. This is called **hydrolysis**. A more extreme example of hydrolysis is given by sodium phosphate (Na_3PO_4) which has strongly basic aqueous solutions:



The $\text{PO}^{3-}_{4(aq)}$ ion is almost as strong a base as $\text{OH}^-_{(aq)}$. Similarly, sodium sulphide (Na_2S) solution is nearly as basic as that of NaOH .

Strong Acid—Weak Base Reactions

This situation is similar to that described above for strong base and weak acid. An example of this is the reaction between an HCl solution and NH_3 :



The $\text{H}_3\text{O}^+_{(aq)}$ is a stronger acid than $\text{NH}^+_{4(aq)}$, yet this reaction is reversible and solutions of NH_4Cl are slightly acidic.

Weak Acid—Weak Base Reactions

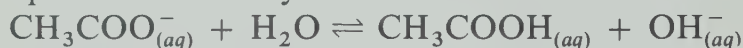
This type of reaction does not proceed to completion—one reactant has little tendency to donate protons and the other has little tendency to accept them. Thus, in the reaction:

$$\text{CH}_3\text{COOH} + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{NH}_4^+_{(aq)}$$

$$\text{weak acid} \quad \text{weak base} \quad \text{strong base} \quad \text{strong acid}$$
 the salt, ammonium acetate ($\text{NH}_4\text{CH}_3\text{COO}$), will decompose in the presence of moisture and even evaporate at room temperature. Solutions of this salt are almost exactly neutral because any tendency of $\text{CH}_3\text{COO}^-_{(aq)}$ ions to remove protons from water is balanced by the tendency of $\text{NH}_4^+_{(aq)}$ ions to donate protons to water.

Hydrolysis

Hydrolysis is an aspect of acid-base equilibrium that traditionally is treated as a separate, distinct phenomenon, but in fact it requires no concepts beyond those we have already discussed. We have remarked that a weak acid and its anion are a conjugate acid-base pair, and that if an acid is weak, its conjugate base tends to be strong. For example, acetic acid is a moderately weak acid, so the acetate ion is a moderately strong base, and will acquire protons in aqueous solution by the reaction:



This reaction represents the hydrolysis of the acetate ion, but we can see that it is nothing more than the “ionization” of a weak base. The equilibrium constant (here called the **hydrolysis constant**) for the reaction above is given by the following expression

$$K_h = \frac{[\text{CH}_3\text{COOH}_{(aq)}] \cdot [\text{OH}^-_{(aq)}]}{[\text{CH}_3\text{COO}^-_{(aq)}]}$$

Hydrolysis constants are not usually tabulated because they can be evaluated from the ionization constants of the corresponding acid. (See the NSCM Core Book C10, *Principles of Chemical Equilibrium*, for more detailed discussion on ionization constants and equilibrium constants.)

Multiplying the above expression by $\frac{[\text{H}_3\text{O}^+_{(aq)}]}{[\text{H}_3\text{O}^+_{(aq)}]}$ we obtain:

$$K_h = \frac{[\text{CH}_3\text{COOH}_{(aq)}] \cdot [\text{OH}^-_{(aq)}] \cdot [\text{H}_3\text{O}^+_{(aq)}]}{[\text{CH}_3\text{COO}^-_{(aq)}] \cdot [\text{H}_3\text{O}^+_{(aq)}]}$$

In the numerator we recognize the product $[\text{OH}^-_{(aq)}] \cdot [\text{H}_3\text{O}^+_{(aq)}]$ which is equal to K_w . This gives us:

$$K_h = \frac{[\text{CH}_3\text{COOH}_{(aq)}] \cdot K_w}{[\text{CH}_3\text{COO}^-_{(aq)}] \cdot [\text{H}_3\text{O}^+_{(aq)}]}$$

but $K_a = \frac{[\text{CH}_3\text{COO}^-_{(aq)}] \cdot [\text{H}_3\text{O}^+_{(aq)}]}{[\text{CH}_3\text{COOH}_{(aq)}]}$

$$\therefore K_h = \frac{K_w}{K_a}$$

at 298 K: K_w is 1.00×10^{-14} and

K_a (CH_3COOH) is 1.85×10^{-5}

$$\therefore K_h = \frac{1.00 \times 10^{-14}}{1.85 \times 10^{-5}}$$

$$= 5.4 \times 10^{-10}$$

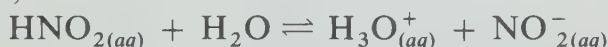
the equation $K_h = \frac{K_w}{K_a}$ can be used more generally than for the example used to derive it.

This equation shows that the weaker the acid the smaller is the value of K_a and the more extensively hydrolysed is the anion.

Relationship between K_a and K_b

In tables 2 and 3, some acid and base constant values are given. Table 2 on page 17 shows the acids listed in order of decreasing strength—table 3 on page 20 shows the bases listed in order of decreasing strength. Let us now study the relationship between the acid equilibrium constant (K_a) and the base equilibrium constant (K_b) for the conjugate base of a particular acid.

For example, nitrous acid reacts with water as follows:

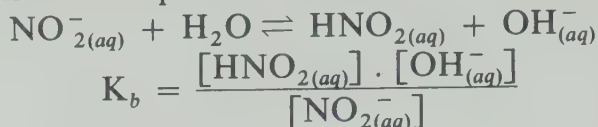


The acid equilibrium expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+_{(aq)}] \cdot [\text{NO}_2^-_{(aq)}]}{[\text{HNO}_{2(aq)}]}$$

The nitrite ion, $\text{NO}_2^-_{(aq)}$, is the conjugate base of nitrous acid.

The base equilibrium expression is based on the following equation:



rearranging the K_a expression:

$$K_a = [\text{H}_3\text{O}^+(\text{aq})] \cdot \frac{[\text{NO}_2^-(\text{aq})]}{[\text{HNO}_2(\text{aq})]}$$

rearranging the K_b expression:

$$\frac{[\text{NO}_2^-(\text{aq})]}{[\text{HNO}_2(\text{aq})]} = \frac{[\text{OH}^-(\text{aq})]}{K_b}$$

combining these two expressions:

$$K_a = [\text{H}_3\text{O}^+(\text{aq})] \cdot \frac{[\text{OH}^-(\text{aq})]}{K_b}$$

$$K_a \cdot K_b = [\text{H}_3\text{O}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$$

$$\text{but } K_w = [\text{H}_3\text{O}^+(\text{aq})] \cdot [\text{OH}^-(\text{aq})]$$

$$\therefore K_a \cdot K_b = K_w$$

This means that at a particular temperature the product of the acid equilibrium constant for an acid and the base equilibrium constant for the conjugate base of that acid is constant.

Table 2 lists the K_a for nitrous acid at 298 K as 5.0×10^{-4}

that is, $K_a(\text{HNO}_2(\text{aq})) = 5.0 \times 10^{-4}$ at 298 K

Table 3 lists the K_b for the nitrite ion at 298 K as 2.0×10^{-11}

that is, $K_b(\text{NO}_2^-(\text{aq})) = 2.0 \times 10^{-11}$

$$K_a \cdot K_b = (5.0 \times 10^{-4}) \cdot (2.0 \times 10^{-11})$$

$$= 1.0 \times 10^{-14} = K_w$$

$$\therefore K_a \cdot K_b = K_w$$

Using the p notation:

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

Exercise

14 The pK values of acetic acid (ethanoic acid), monochloroacetic acid, dichloroacetic acid and trichloroacetic acid are 4.8, 2.9, 1.3 and 0.7 respectively, at 298 K.

- which is the strongest acid?
- calculate the approximate pH of a molar solution of each acid, assuming the acids to be weak.
- can you suggest a reason for the differences between the acids?

Acid-Base Titrations

In many acid-base reactions, the equilibrium is displaced almost completely towards the product side. These reactions are quantitative and can be used as a basis for the analysis of acids and bases.

For example the concentration of an unknown acid may be determined by measuring the volume of a base of known concentration needed to react completely with a specific volume of the acid.

The solution of known concentration is known as a **standard solution**. The process of adding the standard solution from a burette in controlled amounts is called **titration**. In theory, the standard acid is added until the amount of acid is chemically equivalent to the amount of base in the unknown sample. In practice, the point at which chemically equivalent quantities are present, the **stoichiometric point** (also called the *theoretical end point* or *equivalence point*), may be estimated by use of acid-base indicators which change colour at or very near the stoichiometric point. The colour change of an indicator takes place at the end point of the titration. The indicator end point should, in theory, coincide with the stoichiometric point of the reaction.

In practice, however, a very small difference usually occurs; this represents the titration error. We should always endeavour to select an indicator and also the experimental conditions, such that the difference between the visible end point and the theoretical end point is as small as possible.

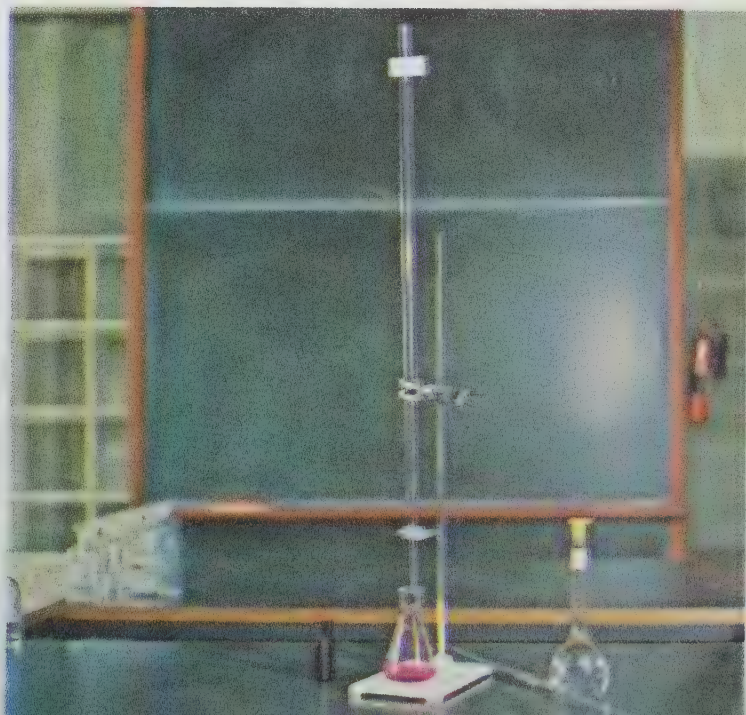


Figure 19. Usual laboratory arrangement for an acid-base titration

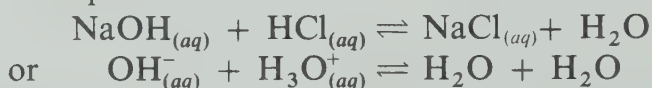
Titration Curves

The choice of indicator for a particular titration depends on the relative strengths of the acid and base involved. The pH at which chemically equivalent quantities of standard and unknown are present, can be calculated or determined from experimentally or theoretically derived titration curves.

An insight into the mechanism of neutralization processes is obtained by studying the changes in the hydronium ion concentration during the course of the appropriate titration. The change in pH in the neighbourhood of the theoretical end point is of the greatest importance as it enables us to select an indicator which will give the smallest titration error.

The curve obtained by plotting pH against the number of ml of alkali added is known as the **titration curve**. This may be determined experimentally by an estimation of the pH at various stages during the titration, using the theoretical principles that we have already studied.

To calculate the pH at the theoretical end point, it is necessary to know the composition of the solution. Consider the titration of 0.10 M HCl aqueous solution, with 0.10 M NaOH aqueous solution. The equation for the reaction:



shows that the reagents react in a one-to-one mole ratio. When chemically equivalent quantities of 0.10 M NaOH and 0.10 M HCl have been reacted, the aqueous solution contains sodium chloride, NaCl.

Titration of Strong Acid with Strong Base

We shall assume that the strong acid, HCl, and the strong base, NaOH, are both completely dissociated in order to calculate the change of pH during the course of the neutralization at room temperature. For simplicity of calculation, we shall begin with 100 ml of the 0.10 M HCl solution. The pH of 0.1 M HCl solution may be calculated as follows:

$$\begin{aligned} [\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \text{ mol l}^{-1} \\ \text{pH} &= -\log [\text{H}_3\text{O}^+_{(aq)}] \\ &= -\log (0.1) \\ &= 1 \end{aligned}$$

When 50 ml of the 0.10 M NaOH solution have been added to the 100 ml of the 0.10 M HCl solution, 50 ml of unreacted acid will be present in the now total volume of 150 ml of solution.

The pH of this solution is as follows:

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \times \frac{50}{150} \\&= 3.33 \times 10^{-2} \text{ mol l}^{-1} \\ \text{pH} &= 1.48\end{aligned}$$

For 75 ml of 0.10 M NaOH solution, 25 ml of unreacted acid remains in 175 ml:

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \times \frac{25}{175} \\&= 1.43 \times 10^{-2} \text{ mol l}^{-1} \\ \text{pH} &= 1.94\end{aligned}$$

For 90 ml of 0.10 M NaOH solution, 10 ml of unreacted acid remains in 190 ml:

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \times \frac{10}{190} \\&= 5.27 \times 10^{-3} \text{ mol l}^{-1} \\ \text{pH} &= 2.3\end{aligned}$$

For 98 ml of 0.10 M NaOH solution, 2 ml of unreacted acid remains in 198 ml:

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \times \frac{12}{198} \\&= 1.01 \times 10^{-3} \text{ mol l}^{-1} \\ \text{pH} &= 3.0\end{aligned}$$

For 99 ml of 0.10 M NaOH solution, 1 ml of unreacted acid remains in 199 ml:

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \times \frac{1}{199} \\&= 5.03 \times 10^{-4} \text{ mol l}^{-1} \\ \text{pH} &= 3.3\end{aligned}$$

For 99.9 ml of 0.10 M NaOH solution, 0.1 ml of unreacted acid remains in 199.9 ml:

$$\begin{aligned}[\text{H}_3\text{O}^+_{(aq)}] &= 0.1 \times \frac{0.1}{199.9} \\&= 5.01 \times 10^{-5} \text{ mol l}^{-1} \\ \text{pH} &= 4.3\end{aligned}$$

Upon the addition of 100 ml of 0.10 M NaOH to the 100 ml of 0.10 M HCl the pH will change sharply to 7, the theoretical end point.

For 100.1 ml of 0.10 M NaOH, 0.1 ml of unreacted alkali remains in 200.1 ml:

$$\begin{aligned}[\text{OH}_{(aq)}^-] &= 0.1 \times \frac{0.1}{200.1} \\&= 5.00 \times 10^{-5} \text{ mol l}^{-1} \\ \text{pOH} &= 4.3 \\ \text{pH} &= 9.7\end{aligned}$$

For 101 ml of 0.10 M NaOH solution, 1 ml of unreacted alkali remains in 200.1 ml:

$$\begin{aligned}[\text{OH}_{(aq)}^-] &= 0.1 \times \frac{1}{201} \\&= 5.00 \times 10^{-4} \text{ mol l}^{-1} \\ \text{pOH} &= 3.3 \\ \text{pH} &= 10.7\end{aligned}$$

These results show that as the titration proceeds, the pH of the solution rises slowly, but between the addition of 99.9 ml and 100.1 ml of 0.10 M NaOH, the pH of the solution rises from 4.3 to 9.7. That is, in the vicinity of the theoretical end point the rate of change of pH of the solution is large. The complete results, extended to 200 ml of the 0.10 M NaOH solution, are collected in table 8.

In quantitative analysis we are especially interested in the changes of pH near the theoretical end point. Figure 20 shows

Table 8. pH during titration of 100 ml of 0.10 M HCl with 0.10 M NaOH

ml of 0.10 M NaOH added	pH of solution	ml of 0.10 M NaOH added	pH of solution
0	1.0	100.1	9.7
50	1.5	100.2	10.0
75	1.8	100.5	10.4
90	2.3	101	10.7
98	3.0	102	11.0
99	3.3	110	11.7
99.5	3.6	125	12.2
99.8	4.0	150	12.5
99.9	4.3	200	13.0
100.0	7.0		

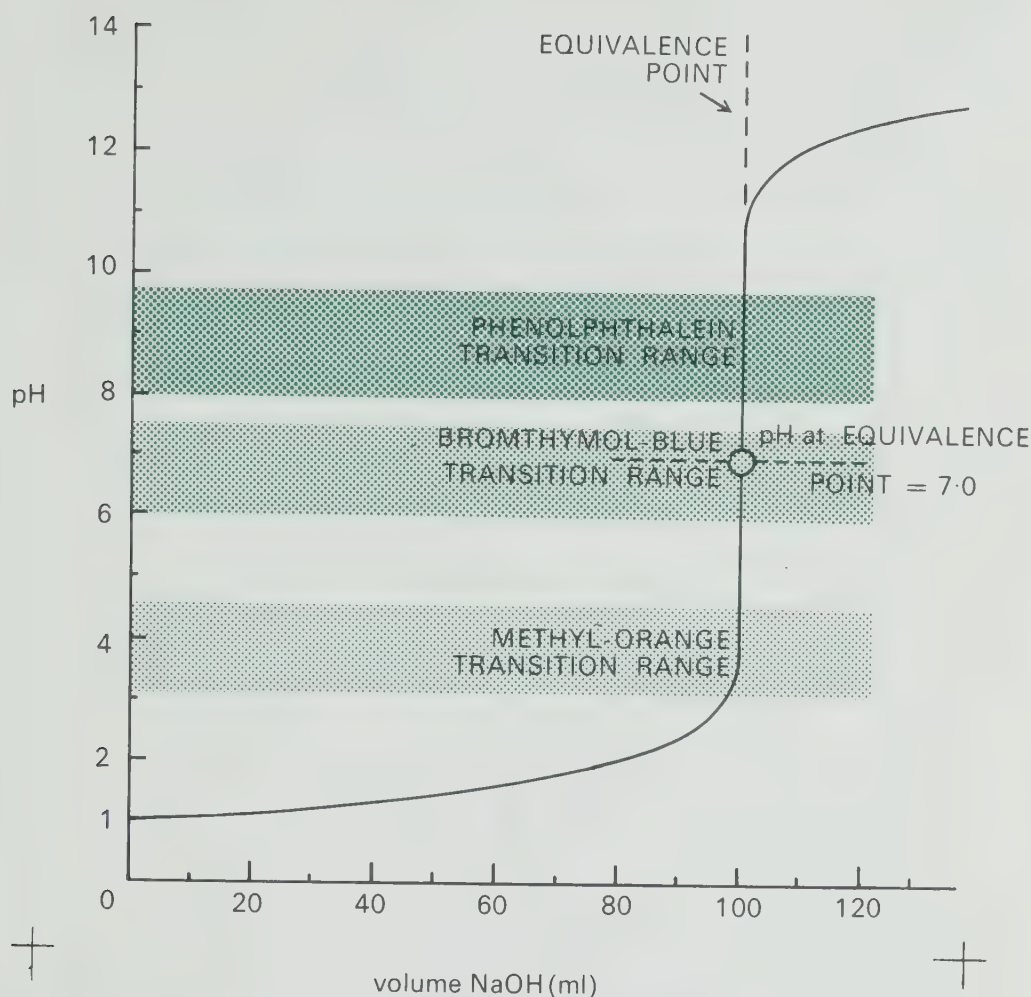


Figure 20. Titration curve for titration of 100 ml of 0.10 M HCl with 0.10 M NaOH

graphically the changes in pH for the above titration, namely 100 ml of 0.10 M HCl with 0.10 M NaOH using bromthymol blue as the indicator. Prior to the end point, the indicator is yellow in the acid solution. A sudden change in the colour of the solution from yellow to green marks the equivalence point (end point) of the titration. One drop past the end point the colour changes to blue indicating an alkaline solution.

Since a drop or two of the 0.10 M NaOH changes the pH by approximately 6 units, any indicator that changes colour between pH 4 and pH 10 could be used to detect the end point in the titration of HCl and NaOH, namely a strong acid with a strong base.

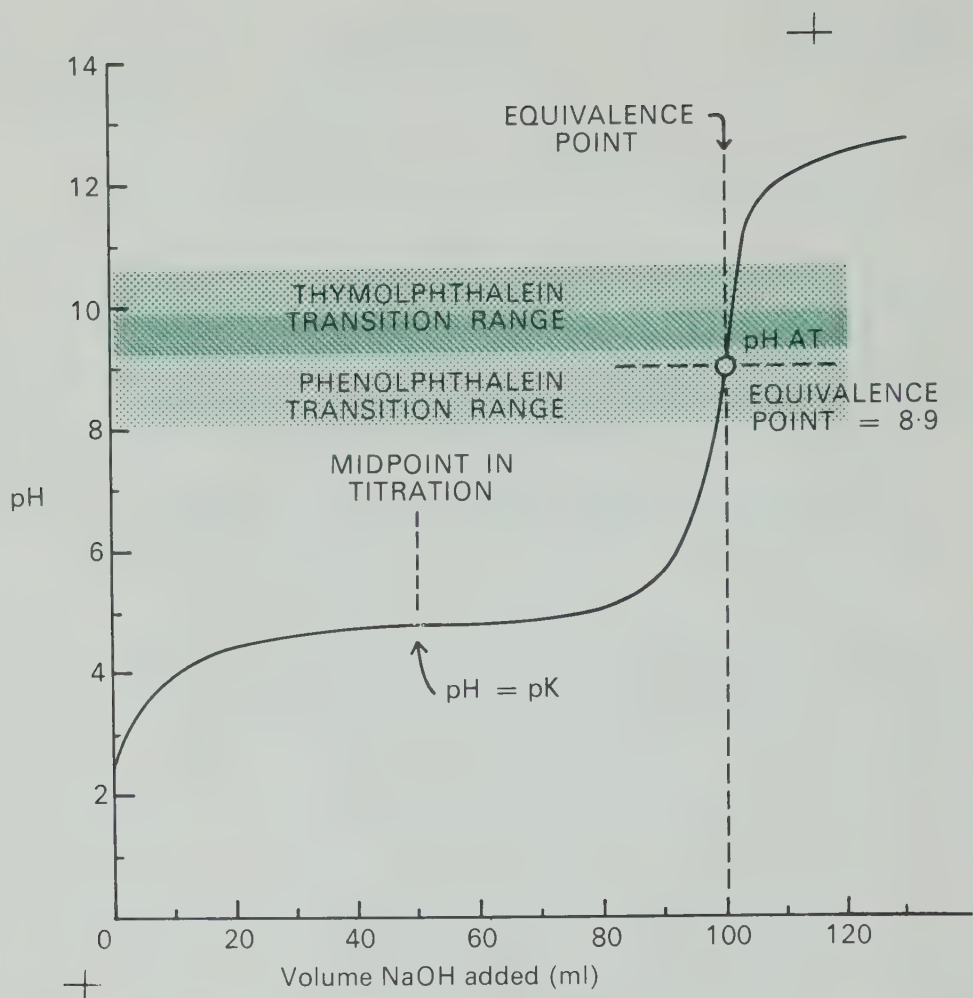


Figure 21. Titration curve for titration of 100 ml of 0.10 M CH_3COOH with 0.10 M NaOH

Titration of Weak Acid with Strong Base

The calculated curve for the titration of 0.10 M CH_3COOH (acetic acid) which is a weak acid, with 0.10 M NaOH, a strong base, is shown in figure 21.

The equivalence point is at a pH of 8.9 and it is necessary to use an indicator which changes colour in the slightly alkaline range, such as phenolphthalein (pH range 8.0–9.6) or thymolphthalein (pH range 9.3–10.5).

Titration of Strong Acid with Weak Base

This case may be demonstrated by the titration of 0.10 M HCl, a strong acid, with 0.10 M NH_4OH , a weak base, as is illustrated graphically in figure 22.

The equivalence point for this titration occurs at a pH of 5.1 and it is necessary to use an indicator with a pH range on the slightly acid side, such as methyl orange (pH range 3.1–4.4) or bromophenol blue (pH range 2.7–4.6).

Titration of Weak Acid with Weak Base

This case is demonstrated by the titration of 0.10 M CH_3COOH with 0.10 M NH_4OH . The pH at the equivalence point is 7.0, and the titration curve is shown in figure 23.

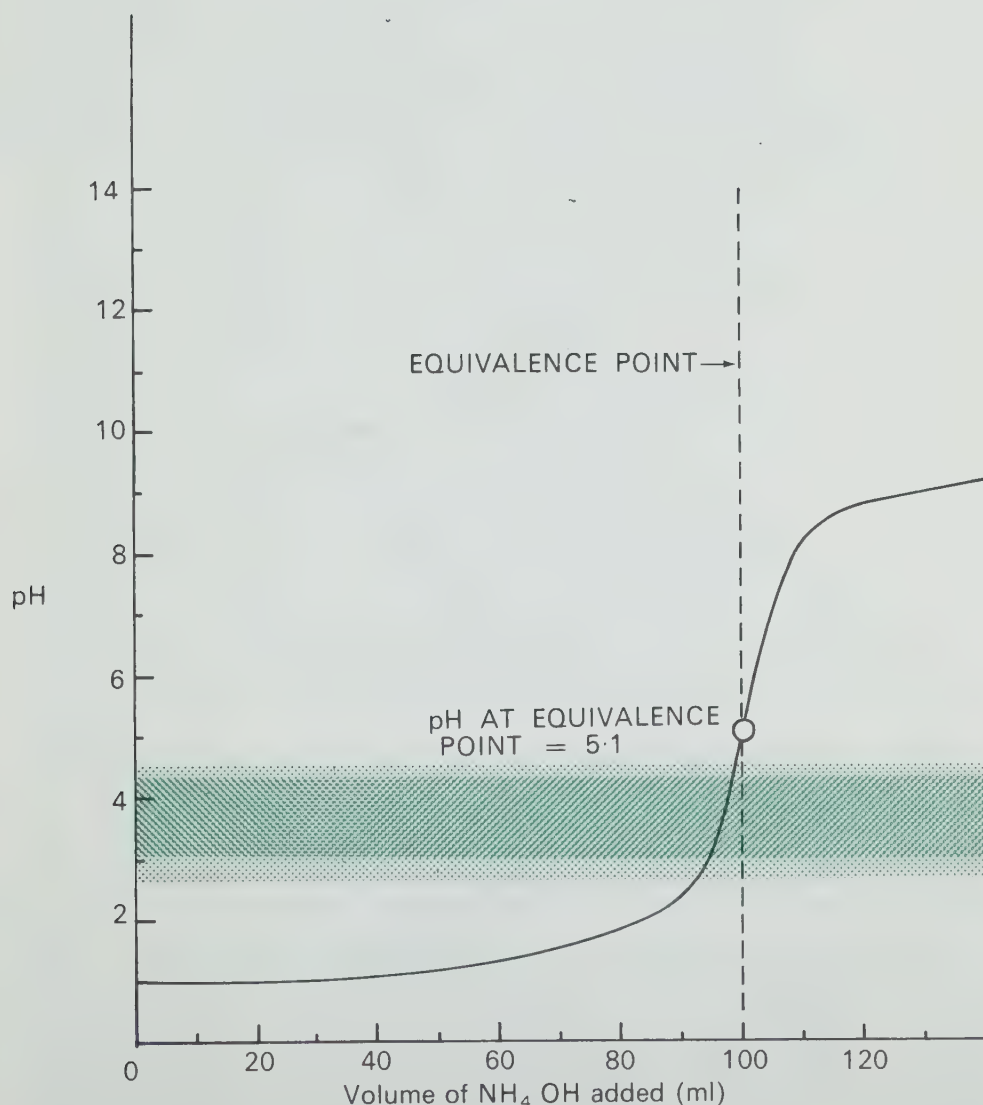


Figure 22. Titration curve for titration of 100 ml of 0.10 M HCl with 0.10 M NH_4OH

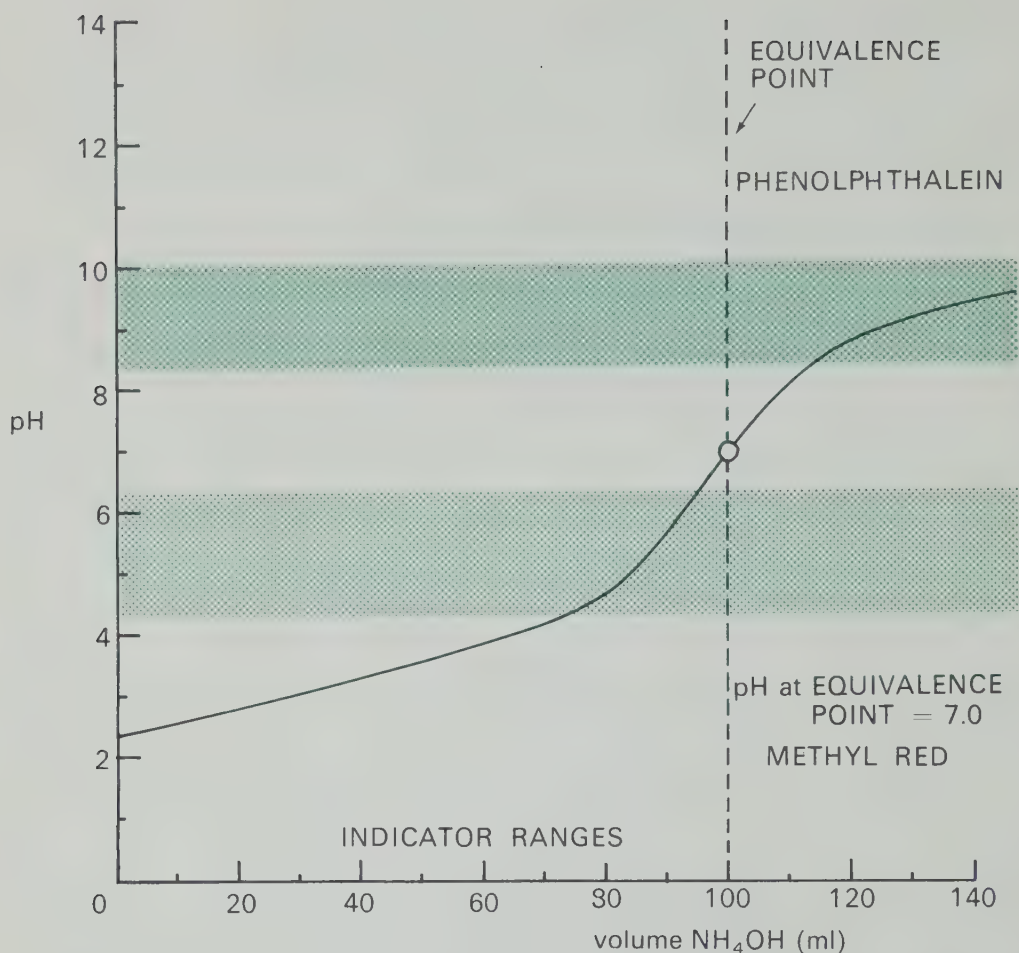


Figure. 23. Titration curve for titration of 100 ml of 0.10 M CH_3COOH with 0.10 M NH_4OH

The main feature of this curve is that the change of pH near the equivalence point, and indeed during the whole of the titration curve, is very gradual. There is no sudden change in pH, and therefore no sharp end point can be found with any simple indicator. On the whole, it is best to avoid titrations involving both a weak acid and a weak base.

Exercises

- 15 A hydrochloric acid solution contains 3.65 g of HCl per litre of solution.
- calculate the molar concentration of this solution;
 - assuming complete dissociation, calculate $[\text{H}_3\text{O}^+_{(aq)}]$;
 - what is the pH of this solution?
 - how many ml of this solution will be required to neutralize 40 ml of 0.20 M NaOH solution?

- 16 Using table 7 choose a suitable indicator for each of the following neutralizations:
- H_2SO_4 and NaOH ;
 - $\text{Ca}(\text{OH})_2$ and CH_3COOH ;
 - HCl and $\text{NH}_{3(aq)}$.
- 17 What volume of 0.10 M HCl solution will be required to neutralize the following solutions?
- 125 ml of 2.0 M Na_2CO_3 solution;
 - 25 ml of 1.0 M NaOH solution;
 - 50 ml of 0.1 M $\text{Ba}(\text{OH})_2$ solution.
- 18 A sample of commercial vinegar was titrated with a standardized NaOH solution to determine the concentration of acetic acid. The following data were obtained:
- | | |
|-------------------------------------|-------|
| volume of vinegar sample | 48 ml |
| volume of 0.40 M NaOH used | 72 ml |
- what indicator might be used to determine the end point of the titration?
 - what is the molarity of the acetic acid?
 - how many g l^{-1} of acetic acid are present in the vinegar?
- 19 A student puts 50 ml of 0.1 M HCl in a beaker and then adds increments of 0.1 M NaOH solution. Compute the pH after the addition of the following volumes of the NaOH solution:
- | | |
|--------------------------------|--------------------------------|
| (a) no NaOH added; | (e) 50 ml NaOH added; |
| (b) 10 ml NaOH added; | (f) 51 ml NaOH added; |
| (c) 25 ml NaOH added; | (g) 55 ml NaOH added. |
| (d) 49 ml NaOH added; | |
- Plot the results, showing pH on the y-axis and volume of NaOH added on the x-axis.
- 20 The following volumes of 0.1 M HCl are added to a beaker that initially contains 50 ml of 0.1 M NaOH solution: 0 ml, 10 ml, 25 ml, 49 ml, 50 ml, 51 ml, 55 ml. Compute the pH after each addition of HCl and plot pH on the y-axis versus volume of HCl on the x-axis; compare the pH curve with that of exercise 19.
- 21 After eating too much pizza, a person prescribes for himself a potion made by dissolving one-quarter teaspoon (0.70 g) of baking soda (NaHCO_3) in a glass of water (250 ml).
- what is the pH in the potion?
 - if this pizza eater drinks 100 ml of the potion and it mixes in his stomach with 100 ml of 0.020 M HCl , what is the pH in there?
- 22
- What is the pH after 25 ml of 0.02 M NaOH is added to 50 ml of 0.1 M HCl ?
 - If 25 ml of 0.16 M NaOH is added to 50 ml of 0.1 M HCl , what is the pH?
 - Find the pH after 26 ml of 0.2 M NaOH is added to 50 ml of 0.1 M HCl .

Electronic Theory of Acids and Bases (the Lewis Theory)

Seven years before the Brönsted-Lowry Proton Theory appeared, an American chemist, G. N. Lewis (1875-1946), had published his theories of chemical bonding, in which he introduced the idea of the covalent bond to explain the structure of non-ionic molecules. The bond between the two atoms in a molecule is pictured as a pair of electrons shared between the atoms. The theory of the covalent bond and the contribution of Lewis is more fully discussed in the NSCM Core Book C2, *Chemical Bonding*.

It will be recalled, that the Brönsted-Lowry concept enlarges the definition of a base more than it does the definition of an acid. According to the Brönsted-Lowry theory, a base is a molecule or ion that has an unshared electron pair with which it can attract and hold a proton; an acid is a substance that can supply a proton to a base.

If a molecule or ion can share an electron pair with a proton, it can do the same thing with other substances as well.

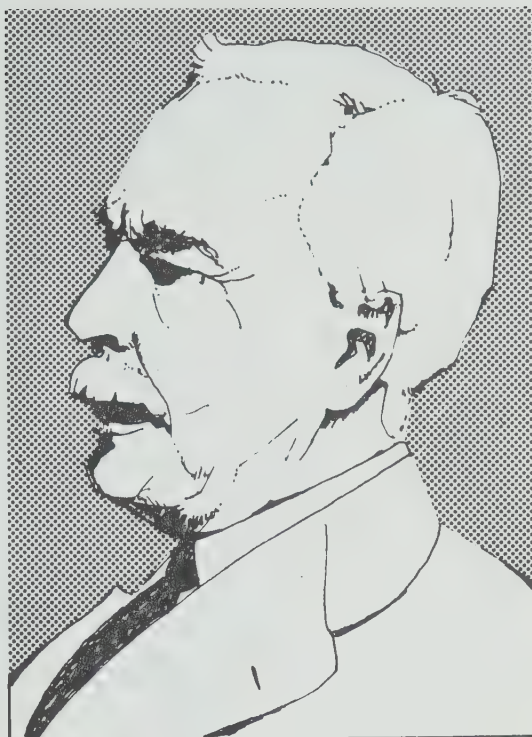
Lewis proposed a broader concept of acids and bases that liberated acid-base reactions from the proton. Although Lewis first proposed his acid-base theory in 1923, he did little to develop it until 1938. According to the Lewis theory:

An acid is any substance (molecule or ion) which can accept a pair of electrons. A base is any substance (molecule or ion) which can donate a pair of electrons.

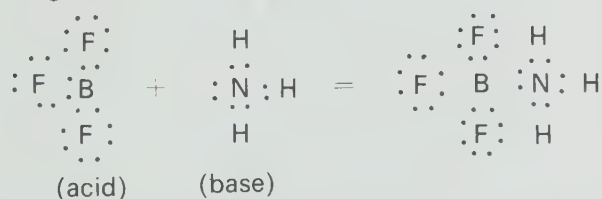
An acid-base reaction, then, consists of the donation of a pair of electrons from the base to the acid with the formation of a coordinate bond between them. (When both the electrons in the pair which is shared between the two atoms come from one of the atoms, the covalent bond formed is often referred to as a coordinate covalent bond or simply as a coordinate bond.)

The Lewis definition of the acid-base reaction includes all the reactions classified as acid-base by the previous definitions, but goes beyond them to include many more. An example of a Lewis acid-base reaction that is not treated as such by any other acid-

Figure 24. Gilbert Lewis (1875-1946) was an American chemist born in Weymouth, Massachusetts. In 1899 he graduated from Harvard University, where he received his doctorate in chemistry, and continued his studies at Leipzig and Göttingen in Germany. He was Professor of Chemistry at the Massachusetts Institute of Technology for five years and was then called to the University of California as Professor of Physical Chemistry. During his thirty years at the University Lewis received much recognition and many honours for his work on the electronic theory of the covalent bond and the electronic theory of acids and bases.

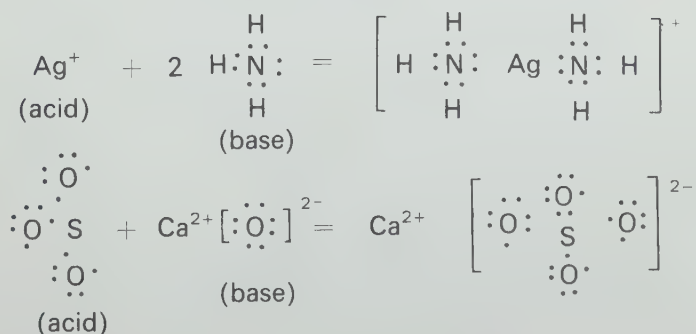


base concept, is the reaction between ammonia and boron trifluoride. (See figure 25.)



Many Lewis acids and bases of this type can be titrated against one another by the use of suitable indicators in the same way that “traditional acids and bases” can be titrated.

The equations in figure 26 show the more general application of the acid-base theory as proposed by Lewis:



A little reflection will reveal that a substance that qualifies as a Brönsted-Lowry base will also be a Lewis base. **In order to accept a proton a substance must donate a pair of electrons.**

When ammonia reacts with water to form the ammonium ion, as shown in figure 27, ammonia is acting as both a Brönsted-Lowry base and a Lewis base:



The water molecule can act as a Brönsted-Lowry acid but not as a Lewis acid. Recall that a Lewis acid is capable of accepting a pair of electrons, but the water molecule has no electron-pair vacancies—it is electronically satisfied. Could the hydrogen ion transferred from water to the ammonia molecule be considered a Lewis acid? Some examples illustrating the Lewis acid-base theory are given in table 9.

Table 9. Lewis acids and bases

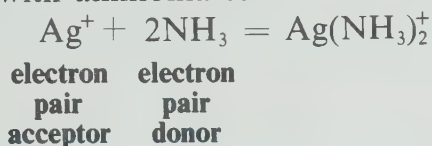
Lewis acids	Lewis bases
Cations, e.g. H^+ , Ag^+ , Cu^{2+} , NO_2^+	Anions, e.g. OH^- , Cl^- , H^-
Molecules in which an atom has an unsaturated valence shell, e.g. BF_3 , AlCl_3 , SiCl_4	Molecules in which an atom has one or more unshared electron pairs in its valence shell, e.g. H_2O , NH_3 .

Lewis acid-base reactions

Lewis Acid	Lewis Base	Product
F_3B	$+$ $:\text{NC}_5\text{H}_5$	$\rightleftharpoons \text{F}_3\text{B}:\text{NC}_5\text{H}_5$
S	$+$ $:\text{S}^{2-}$	$\rightleftharpoons [\text{S}:\text{S}]^{2-}$ or S_2^{2-}
SO_3	$+$ $:\text{O}^{2-}$	$\rightleftharpoons [\text{O}:\text{SO}_3]^{2-}$ or SO_4^{2-}
Ag^+	$+$ $2:\text{CN}^-$	$\rightleftharpoons [\text{NC}:\text{Ag}:\text{CN}]^-$ or $\text{Ag}(\text{CN})_2^-$

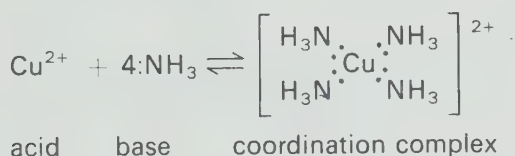
Formation of Complex Ions

The formation of complex ions involves coordinate bond formation and may be classified as Lewis acid-base reactions. The silver ion reacts with ammonia to form the diamminesilver ion—

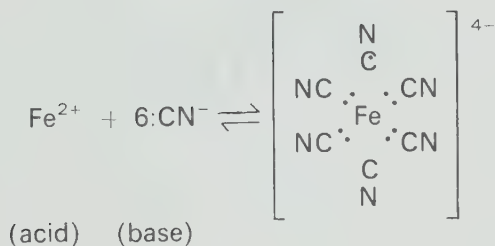


The central cation of a complex ion is a Lewis acid capable of accepting a pair of electrons; the ammonia is the Lewis base.

Other examples of the formation of complex ions are:



and



A generalization from the formation of complex ions is—**simple cations may act as Lewis acids**. All simple cations have an empty orbital in their outer energy level and can, in theory, act as Lewis acids. For example, the Al^{3+} ion in an aqueous solution reacts with 6 water molecules to form the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion. The 6 water molecules each donate a pair of electrons to the Al^{3+} ion. Therefore the water molecules act as Lewis bases and the Al^{3+} ion acts as a Lewis acid. As explained on page 12 the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion acts as a Brönsted-Lowry acid.

Molecules having a central atom with an incomplete octet or containing multiple bonds may act as Lewis acids.

Boron trifluoride, BF_3 , was shown earlier in the reaction with ammonia, NH_3 , to form BF_3NH_3 . Boron has an incomplete octet of electrons but still acts as a Lewis acid. The reaction of

calcium oxide, CaO , with sulphur trioxide, SO_3 , was given earlier as an example of a Lewis acid-base theory. Calcium oxide is a base because it neutralizes a number of common acids. SO_3 behaves as an acid when it neutralizes a number of common bases. Neither the Arrhenius theory nor the Brönsted-Lowry theory classifies SO_3 as an acid, or the reaction under discussion as an acid-base reaction.

Why is SO_3 a Lewis acid? To answer this question we must assume that the pair of electrons donated by the oxide ion forces one pair of electrons in the double bond to shift to one of the oxygen atoms. Since SO_3 accepts an electron pair from CaO , it qualifies as a Lewis acid. Molecules containing multiple bonds between carbon atoms do not behave as Lewis acids. One distinct advantage of the Lewis theory is that it explains the long recognized basic properties of metal oxides like CaO , and the acidic properties of non-metal oxides, such as SO_3 .

A word of warning! We have seen that the Lewis definition of acids does not really represent an extension or generalization of the older theories, but rather the use of the word "acid" in a fundamentally different sense. The most important aspects of the traditional acid-base concepts are the quantitative relationships to which they lead. No such general quantitative treatment can be envisaged for Lewis acids. The protonic acids make up a group which show greater uniformity than do the non-protonic acids of the Lewis definition.

Exercises

- 23 NH_4Cl reacts with sodium amide, NaNH_2 , in liquid ammonia to produce sodium chloride and ammonia. Interpret this reaction in terms of the Brönsted-Lowry and Lewis theories of acids and bases. State clearly what acid(s) and base(s) are involved in each case.
- 24 Classify the following substances as either electron donors or electron acceptors (Lewis bases and acids).
- | | |
|---|---------------------------|
| (a) ammonia | (d) silicon tetrafluoride |
| (b) sulphur dioxide | (e) Cr^{3+} ions |
| (c) ether, $(\text{C}_2\text{H}_5)_2\text{O}$ | (f) I^- ions. |

Usanovich Theory of Acids and Bases

Although the definitions of Arrhenius, Brönsted-Lowry, and Lewis are the most commonly used, there have been several additional classifications proposed for the interpretation of acid-base behaviour. Of these, perhaps the most significant is the positive-negative definition given in 1939 by the Russian chemist, M. Usanovich, in which an acid is **defined as any species capable of giving up cations, combining with anions or electrons, or neutralizing a base to give a salt.**

A base is defined as any species capable of giving up anions or electrons, combining with cations, or neutralizing an acid to give a salt.

The Usanovich definition includes all previous acid-base definitions, as well as including oxidation-reduction reactions as a special class of acid-base reactions. It is capable of correlating a vast number of reactions under the classification of acid-base. However, if we accept the Usanovich definition, we find that virtually all chemical reactions fall into the acid-base category, and one begins to wonder at the purpose of using any name other than chemical reaction.

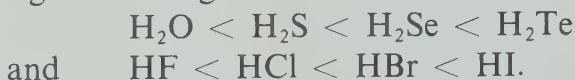
Acid and Base Strengths and Structure

The correlation between molecular structure and acid or base strength is complex and involves many factors. Polar molecules with a hydrogen atom situated at the positive end of the dipole are acids. In such molecules, electrons are withdrawn from the hydrogen atom, thereby facilitating its release as a proton.

For the hydrogen compounds of the elements of a given period of the periodic table, increasing acid strength parallels increasing electronegativity of the atom combined with hydrogen. For the elements of the second period, the order of increasing acid strength of the hydrogen compounds of the last three elements is:

NH_3 is a weaker acid than H_2O ;
 H_2O is a weaker acid than HF ;
that is, $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$.

However, increasing acid strength does not always parallel increasing electronegativity of the atom bonded to hydrogen; evidently other factors are also involved. There is an increase in acid strength of the hydroacids of the elements in any group of the periodic table of the elements with increasing atomic size of the electronegativity element. For example, the hydrogen compounds of group VI and group VII elements arranged according to increasing acid strength are:



In each series, the last compound is the strongest acid and is formed by the element of lowest electronegativity.

Conclusion

Each of the acid-base theories mentioned in this book presents certain difficulties, and a practical point at issue is, which theory is able to clearly and quantitatively assist in calculation involving acid-base systems. It should be emphasized that there is no one definition of acids and bases that replaces all the rest. Each of the three concepts has its merits. The reader should be familiar with all three theories and use one that best fits the situation at hand.

The Arrhenius theory restricts acids and bases to those substances which produce, by dissociation, hydrogen ions and hydroxyl ions respectively.

The Brönsted-Lowry theory uses essentially the same meaning for an acid, but widens the definition of a base to include all substances with reactive unshared electron pairs which can react with a proton.

The Lewis theory in turn uses the Brönsted-Lowry meaning for a base, but widens the definition of an acid to include any substance which can form a coordinate bond with an unshared electron pair of a base.

Table 10. Summary of acid-base theories

Theory	Acid	Base
Arrhenius (in water only)	substances which furnish hydrogen ions (protons) in water solution	substances which furnish hydroxide ions in water solution
Brönsted-Lowry (in any solvent)	substances which donate protons (may or may not be in water solution)	substances capable of accepting protons
Lewis (in any solvent)	electron-pair acceptors (may or may not contain protons)	electron-pair donors

A chemical theory is judged by its usefulness and is discarded when it is replaced by a theory of greater usefulness. All three of these acid-base theories are in current use because each can be applied with benefit to appropriate systems. The problem is similar to that of a man choosing a tool to cut a piece of wood. He might use a knife, a plane, or a saw. Any one of the three tools can cut wood, but each is best suited to a certain kind of cutting.

All of the various definitions of acids and bases have a certain use and where it may be convenient to use one particular definition it may not be convenient to use another. From the basic nature of a definition, it is obvious that the question of validity does not enter. The problem is one of choosing which acid-base definition will be of the greatest value for the particular problem.

Reading List

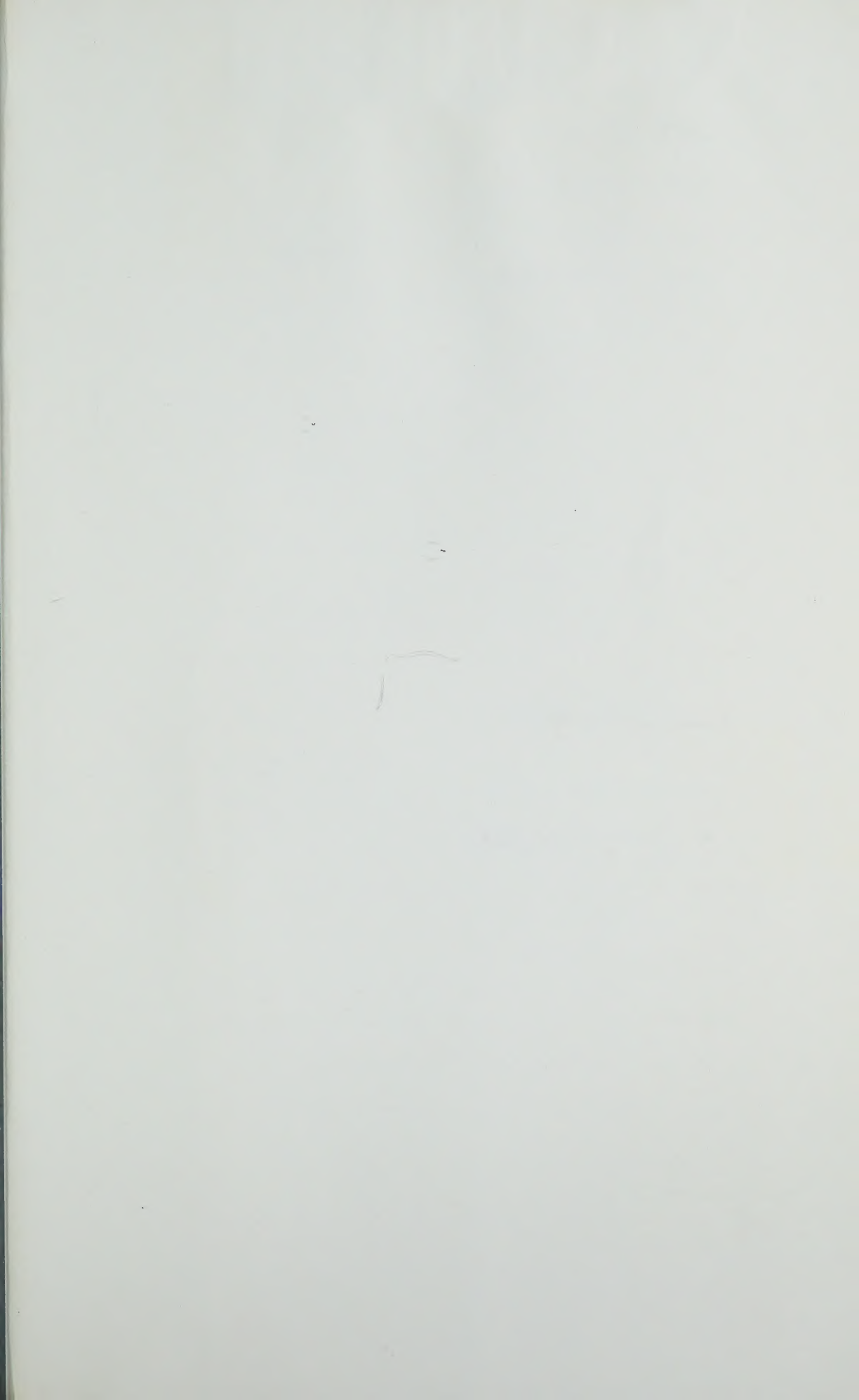
- Cotton, F. A. and Lynch, L. D. 1968. *Chemistry: an Investigative Approach*. Boston: Houghton Mifflin. Chapter 16 applies equilibria principles to acids and bases in a style capable of being understood by the average high-school student.
- Gray, H. B. and Haight, G. P. 1967. *Basic Principles of Chemistry*. New York: W. A. Benjamin. Chapter 15 is suitable for further study in acid-base theory.
- King, E. J. 1965. *Acid-Base Equilibria*. New York: Macmillan. A sophisticated approach to acid-base theory, small sections of the book suitable as background reading.
- Luder, W. F. and Zuffanti, S. 1961. *The Electronic Theory of Acids and Bases*. New York: Dover. If further background reading is required this paperback is recommended.
- Parry, R. W. et al. 1970. *Chemistry—Experimental Foundations*. Englewood Cliffs, N.J.: Prentice-Hall. The philosophy of CHEM Study as applied to this theory is well presented in chapter 13.
- Toon, E. R. et al. 1968. *Foundations of Chemistry*. New York: Holt, Rinehart & Winston. Chapter 15 covers the acid-base theory but in less detail than that presented in this NSCM Project book.
- Vanderwerf, C. A. 1961. *Acids, Bases and the Chemistry of the Covalent Bond*. New York: Reinhold. The first 40 pages gives an easy to read review of this theory.

Revision Questions

- 1 When NaHCO_3 is heated; H_2CO_3 and Na_2CO_3 are formed. Show how this may be treated as an acid-base reaction with $\text{HCO}_3^-_{(aq)}$ acting as both acid and base.
- 2 Write the acid-base reaction for the hydrolysis of Na_2S .
- 3 Write the two successive acid-base reactions which occur when concentrated sulphuric acid (H_2SO_4) is dissolved in water.
- 4 Treat the slaking of lime ($\text{CaO} + \text{H}_2\text{O}$) as an acid-base reaction using $\text{Ca}^{+2}_{(aq)}$ as spectator ion. What does this reaction indicate about the strength of the $\text{O}^{-2}_{(aq)}$ ion as a base?
- 5 When magnesium is burned in nitrogen, magnesium nitride forms. This magnesium nitride will react with water to form NH_3 and $\text{Mg}(\text{OH})_2$. How does the base strength of the nitride ion ($\text{N}^{-3}_{(aq)}$) compare with that of the $\text{OH}^-_{(aq)}$ ion? Is NH_3 an acid or base in this reaction?
- 6 Smelling salts are crystals of ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$. They smell strongly of ammonia. How can this be explained in terms of Brönsted-Lowry theory?

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R. T. Slattery, B.Sc., A.S.T.C., A.R.A.C.I., M.A.C.E.

Ray Slattery was full-time director of the NSCM Project for several years and is still working for NSCM in a part-time capacity. For many years he was a senior science and mathematics master in schools of the A.C.T. and Queensland. He has conducted in-service teacher courses for CHEM Study in Queensland, Tasmania and New South Wales. In 1964 he was awarded the A.I.D.A. medal for his contributions to science teaching, especially in the preparation of teachers involved in the implementation of new curricula and in 1967 he was granted a Churchill Fellowship to study science education technology in the U.S.A. and Canada. His present position is Secretary of the N.S.W. Catholic Education Board.

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